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DEVELOPMENT OF A THIN FILM  
SOLID STATE GASEOUS HCl SENSOR

By Solid State Laboratory  
Department of Electrical Engineering



Prepared under Contract No. NAS1-12833 by  
NORTH CAROLINA STATE UNIVERSITY  
Raleigh, NC 27607

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

## Foreward

This research effort was performed in the Solid State Laboratory at North Carolina State University under the direction of Dr. L. K. Monteith. This report is based upon the research of M. L. Timmons, Research Assistant, and Dr. P. K. Ajmera, Research Associate, who also cooperated in the writing of this report.

Previous work at North Carolina State University on which much of this effort is based is reported in the Ph.D. thesis of Dr. James Yen, "An Investigation of the Electrical Properties of Zinc Oxide Thin Films Influenced by Oxygen Adsorption", North Carolina State University (1973) and Dr. C. E. Weitzel "Changes in the Photoconductivity of Sputtered Films of Cadmium Sulphide Resulting from Oxygen or Sulfur Dioxide Chemisorption", North Carolina State University (1973).

# TABLE OF CONTENTS

	Page
FORWARD .....	ii
LIST OF TABLES .....	iv
LIST OF FIGURES .....	v
1. INTRODUCTION .....	1
2. MEASUREMENT SYSTEMS AND GAS DELIVERY SYSTEM .....	3
2.1 The DC Measurement System .....	3
2.2 The AC Measurement System .....	6
2.3 Gas Delivery System .....	8
3. MATERIALS EXAMINED .....	13
3.1 Zinc Oxide (ZnO) .....	13
3.2 Tin Oxide (SnO <sub>2</sub> ) .....	14
3.3 Cadmium Sulfide (CdS) .....	16
3.4 Silver Halides .....	17
3.4.1 Silver Chloride (AgCl) .....	17
3.4.1a Film Preparation and Study Using DC Measurements .....	17
3.4.1b AC Measurement Work .....	27
3.4.2 Silver Bromide (AgBr) .....	33
4. FEASIBILITY OF INSTRUMENTATION .....	34
4.1 Temperature .....	34
4.2 Power Supply .....	34
4.3 Signal to Noise Ratio .....	35
4.4 Sampled Gas Flow Rate .....	35
4.5 Response Time .....	36
4.6 Responsivity .....	36
5. APPENDIX .....	40
6. SUMMARY AND RECOMMENDATIONS .....	48
7. REFERENCES .....	49

# LIST OF TABLES

	Page
3.1-1 Response of ZnO to HCl .....	13
3.4-1 Two Cycles of HCl Exposure of 850Å Sample at T=150°C .....	26
3.4-2 Exposure Data for 400Å AgCl Films at Room Temperature .....	26
3.4-3 Results of $R_o$ and $E_a$ Measurements .....	29
3.4-4 Exposure Data for (a) 2200Å AgCl Films, (b) 700Å AgCl Films, and (c) 300Å AgCl Film (HCl in N <sub>2</sub> Ambient) .....	30
3.4-5 Response of AgCl Films (Doped with 250Å CdCl <sub>2</sub> ) to 30% HCl at 400°K .....	32
3.4-6 Exposure Data for (a) 400Å AgCl Film Doped with 250Å CdCl <sub>2</sub> , (b) 400Å AgCl Film Doped with 70Å CdCl <sub>2</sub> at 400°K .....	33
4-1 Exposure Sequence of 400Å AgCl, 70Å CdCl <sub>2</sub> Film .....	38
4-2 Exposure Data of Fresh CdCl <sub>2</sub> -doped AgCl Films .....	39
5-1 Total and Percent Changes in the Film Conductance as a Function of Three Different Temperatures on Exposure to 6000 ppm HCl in 0.5 l/m N <sub>2</sub> Gas Flow .....	43

# LIST OF FIGURES

	Page
2.1 The DC Measurement System .....	4
2.2 The AC Measurement System .....	5
2.3 Phasor Diagram for Measurement Circuit Analysis .....	6
2.4 Gas Delivery System .....	9
2.5 Test Envelope .....	10
2.6 Flowmeter Calibration for the HCl Gas Flow .....	12
3.1 The Effect on ZnO Films to Brief Exposures to 10% HCl in N <sub>2</sub> Concentration at 230°C and 300°C .....	15
3.3-1 Surface Damage to 500Å CdS Film After Exposure to 10% HCl in N <sub>2</sub> at 140°C .....	18
3.4-1 Sample Geometry .....	19
3.4-2 Resistivity of 850Å AgCl Film vs. Temperature in Atmosphere with 20 Volt dc Bias .....	21
3.4-3 Resistivity vs. Temperature of 850Å AgCl Film with 20V dc Bias Under N <sub>2</sub> Ambient .....	22
3.4-4 Example of Cathodic Dendrite Growth on AgCl Film with 20V dc Bias .....	23
3.4-5 Exposure of 850Å AgCl Film to HCl at 100°C .....	25
3.4-6 Resistance vs. Temperature in Vacuum for Unannealed 3300 Å Evaporated AgCl Film .....	28
4.1 Rise Time vs. HCl Concentration .....	37
5.1 Variation of MnO <sub>2</sub> Film Resistance with N <sub>2</sub> Gas Flow Rate at 300°C .....	41
5.2 Percent Change in the Film Conductance as a Function of HCl Concentration in 0.5 l/m N <sub>2</sub> Flow at 300°C .....	44
5.3 Change in the Film Conductance $\sigma$ with Time on Exposure to 6000 ppm HCl in 0.5 l/m N <sub>2</sub> Flow at 300°C .....	45
5.4 Change in the Film Conductance $\sigma$ with Time on Shutting Off 18,000 ppm HCl in 0.5 l/m N <sub>2</sub> Flow at 300°C .....	46

## 1. Introduction

This report summarizes the first phase of a research effort devoted to the development of a thin film solid-state gaseous HCl sensor. The principle of transduction involves the adsorption of HCl onto the surface of a thin semiconducting film which results in a change in surface conductivity of the film. Assuming the film thickness is properly chosen the modulation of surface conductivity can be observed as a terminal characteristic thru an electrical measurement.

To achieve a thin film sensor for HCl vapor the matters of primary concern are the preparation of thin films with suitable physical and chemical properties and with electrical properties which exhibit an enhanced electrical response when HCl is absorbed on the surface of the thin film. The term enhanced should be contrasted with the word specific. Our objective has been to seek methods of enhancing the response of a thin film to HCl and may or may not provide specificity (response is greater for HCl than for other gases). The techniques investigated for enhancement have included the conditions for growing films, adding impurities to the film, changing ambient light intensity and altering the ambient temperature of the sensing element. The criteria for choosing the materials used in this study were:

1. The thin films must be relatively easy to fabricate by vapor deposition technologies.
2. The resistivity of the film may be altered by changing deposition parameters, by introducing impurities or by changing the ambient light intensity and/or ambient temperature of the fabricated film.

3. The resistivity of the vapor deposited semiconductor films can be dominated by vacancy diffusion of a principal molecule of the gas to be monitored. (Silver is the mobile species in AgCl, however it may react with free chlorine at the surface).
4. The resistivity of the vapor-deposited film should be relatively high.
5. The environment should not etch the film or form stable chemical compounds on the surface.

The first phase of the research has focused on the following:

1. Vapor deposition of thin films of wide-band gap compound semiconductors principally oxides and chlorides that are chemically stable in an HCl environment,
2. Determination of electrical and physical properties of evaporated and sputtered thin films to obtain conductivity modulation by chemisorption of HCl,
3. Exposure of thin-films to various concentrations of HCl in a controlled environment and determination of changes in conductivity with changes in HCl concentrations,
4. Characterization of operating conditions such as sensor temperature, applied voltage and gas flow rate necessary to obtain suitable response.
5. Identification of interference effects from water vapor and oxygen.

## 2. Measurement Systems and Gas Delivery System

The nature of the materials which have been examined in the current research effort have required both ac and dc measurement systems. The dc system was used primarily for materials which exhibited electronic conductivity, while the ac system, although applicable to both types of conductivity, was used for the AgCl work where ionic conductivity dominated electronic conductivity. This section describes the systems, presenting schematic drawings of each. It concludes with a description of the gas delivery system and the method used to ascertain HCl concentrations.

### 2.1 The DC Measurement System

The dc measurement system was used during the examination of ZnO, CdS, and SnO<sub>2</sub> materials showing electronic conductivity and for the early work on AgCl. Because of problems discussed in Sec. 3.4.1a, the AgCl work required transition to an ac system. A diagram of the dc system is shown in Fig. 2.1.

The dc system was composed of a battery bank (Duracell, 4.05v, Mercury) connected in series so that potentials in  $\approx 4V$  increments could be applied to the sample films. The polarity reversing switch was used to check the ohmicity of the film contacts in the range of -20 to +20 volts. The current was measured with a Keithley Model 602 Solid State Electrometer, the results being recorded on a Varian Model G 4000 Strip Chart Recorder. The position of the electrometer in the circuit was found to be important and was placed in this particular configuration to minimize the measurement of battery leakage. With the circuit, as shown, satisfactory measurement was achieved for current levels on the order of  $10^{-10}$  amps (this corresponds to film resistances of  $4-20 \times 10^{10}$  ohms).



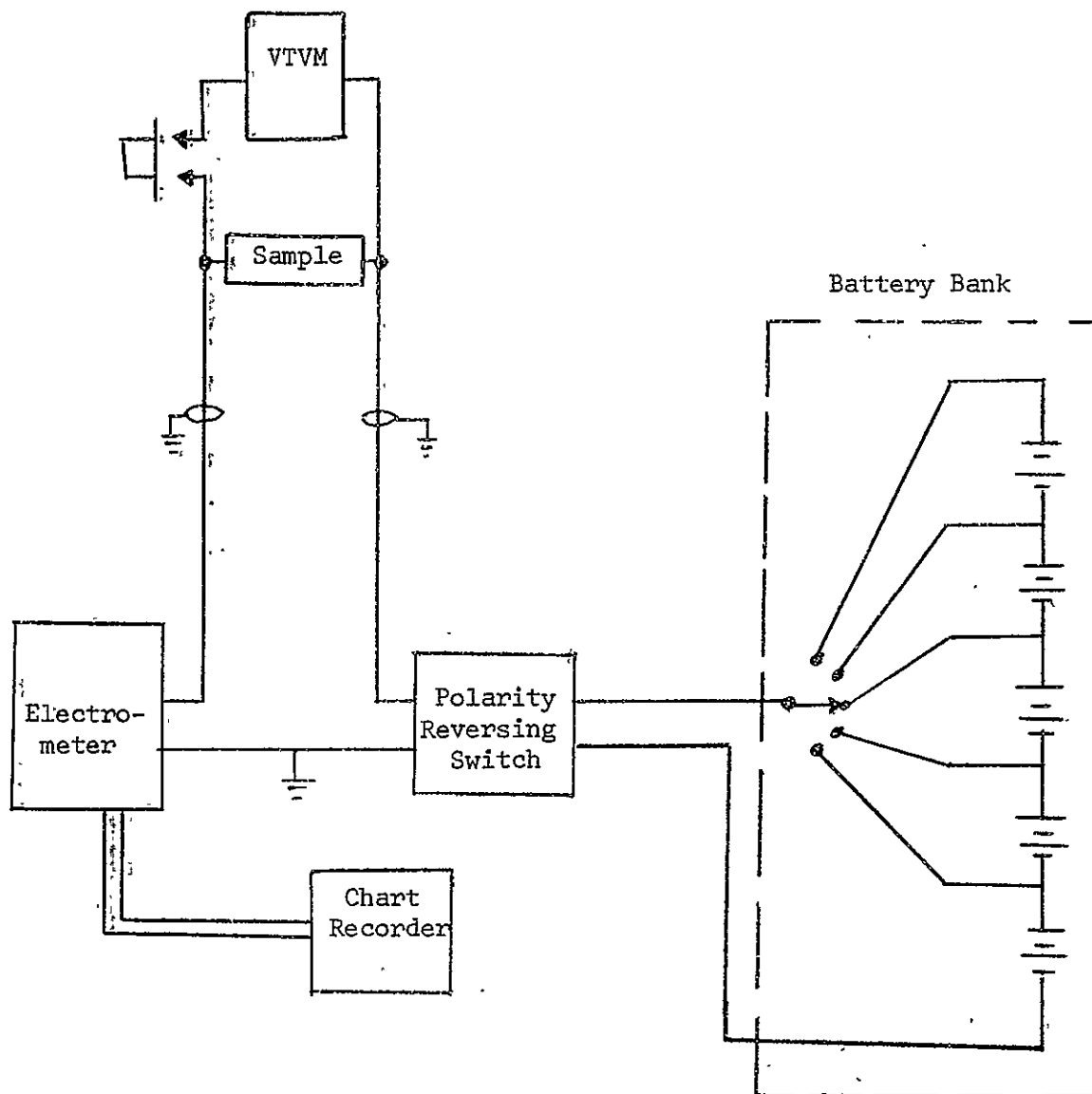


Figure 2.1 The DC Measurement System

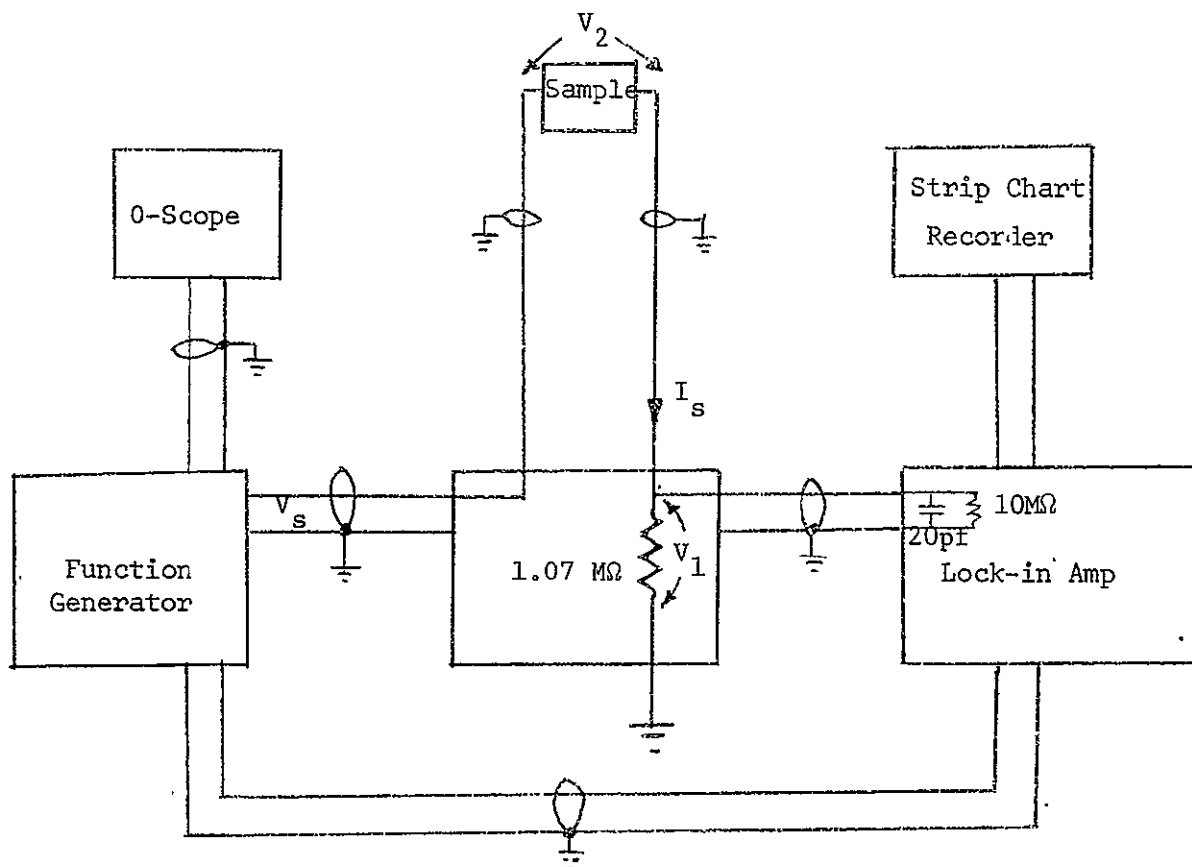


Figure 2.2 The AC Measurement System

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## 2.2 The AC Measurement System

As mentioned earlier, the ac system was more versatile because of its capability of accommodating the electronic- and the ionic-conductivity dominated materials. It also measured the film capacitance values directly. The system design is shown in Fig. 2.2.

The key to the system is the lock-in amplifier. A 1.6Hz signal from the function generator (600 ohm output impedance) is applied to the sample and reference resistor (1.07 Megohm, 1%). The voltage across the standard resistor was measured by the lock-in amplifier (nominal input impedance of 10 megohm shunted by 20 pf - manufacturer's specifications). The amplifier reference signal was taken from the function generator so that the phase shift between the function generator voltage and the measured voltage was read from an amplifier panel dial (accurate to within 5% or 5°, taking the smaller values - manufacturer's specifications). We feel that this is a more convenient measurement system than the use of a capacitance bridge, the prevailing method for materials such as AgCl. The circuit analysis follows:

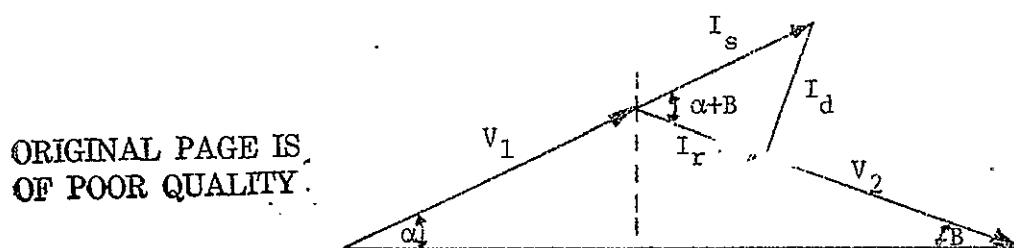


Figure 2.3. Phasor Diagram for Measurement Circuit Analysis (not drawn to scale).

where  $v_s$  = function generator source voltage,

$v_1$  = measured voltage,

$v_2$  = voltage across sample,

$\alpha$  = measured angle between  $v_s$  and  $v_1$ ,

$I_s$  = total current through sample,

$I_r$  = sample resistive current (also system leakage), and

$I_d$  = sample displacement current (also includes any system displacement leakage).

It is obvious from Figure 2.3 that

$$\tan B = \frac{v_1 \sin \alpha}{v_s - v_1 \cos \alpha} \quad (2.2-1)$$

and therefore

$$\beta = \tan^{-1} \left[ \frac{V_1 \sin \alpha}{V_s - V_1 \cos \alpha} \right] \quad (2.2-2)$$

Since

$$V_2 = \frac{V_s - V_1 \cos \alpha}{\cos \beta} \quad (2.2-3)$$

for small  $\beta$  values (less than  $26^\circ$  where  $\cos \beta \approx 0.9$ ) and for  $V_1 \ll V_s$

$$V_2 \approx V_s. \quad (2.3-3)$$

Considering the current  $I_s$  in Figure 2.2

$$I_s = V_1 / 1.07 \text{ M}\Omega \parallel 10 \text{ M}\Omega \quad (2.3-4)$$

$$\approx V_1 / 1.07 \text{ M}\Omega. \quad (2.3-5)$$

and from Figure 2.3

$$I_r = I_s \cos(\alpha + \beta), \quad (2.3-6)$$

or for small  $\beta$ ,

$$I_r \approx I_s \cos \alpha. \quad (2.3-7)$$

In equation (2.3-4) the 20 pf shunting capacitance of the lock-in amplifier is ignored because at 1.6 Hz it offers an impedance in the range

of  $10^9$  ohms. By open circuiting the sample path all measurable leakage was found to be displacement current, implying  $I_r$  is the actual value of resistive current in the sample.

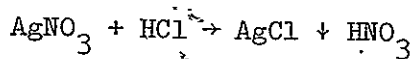
It should be pointed out that the selection of the ground point is quite important in minimizing stray pick-up and leakage measurement. This systems ground point was chosen in according with suggestions in Morrison's Grounding and Shielding Techniques in Instrumentation [1].

With the ac system, resistances in the  $10^{10}$ -ohm range were reliably measured. The limiting factor appeared to be system noise and leakage.

### 2.3 Gas Delivery System

The gas flow system was relatively simple (Fig. 2.4). Inlet ports for HCl and  $N_2$  (or air) are provided with the flow controlled by rotameter-type flowmeters. Two sources of HCl were used. High concentrations (0.1% and up) were achieved by dilution of the pure gas, and lower concentrations ( $\approx 0.01\%$  and down) were achieved by dilution of a commercially prepared 84 part per million HCl/ $N_2$  mixture. Two small volume mixing chambers were provided to assure as homogeneous a mixture as possible. The gas outlet emptied into a base-filled bubbler for neutralization purposes. Figure 2.5 shows details of the test chamber.

Knowing the HCl concentration arriving at the sample during a given measurement is obviously important. A gravimetric analysis was chosen to determine the relationship between gas flow rate into the system and HCl concentration at the sample. A 10% (weight-to-volume) solution of silver nitrate ( $AgNO_3$ ) was prepared. Selected values of HCl flow (determined by flowmeter) were diluted with 0.2 l/min.  $N_2$  flow. These mixtures were bubbled through a network of three cascaded bubblers, filled with the  $AgNO_3$  solution, for a known length of time. The traditional reaction



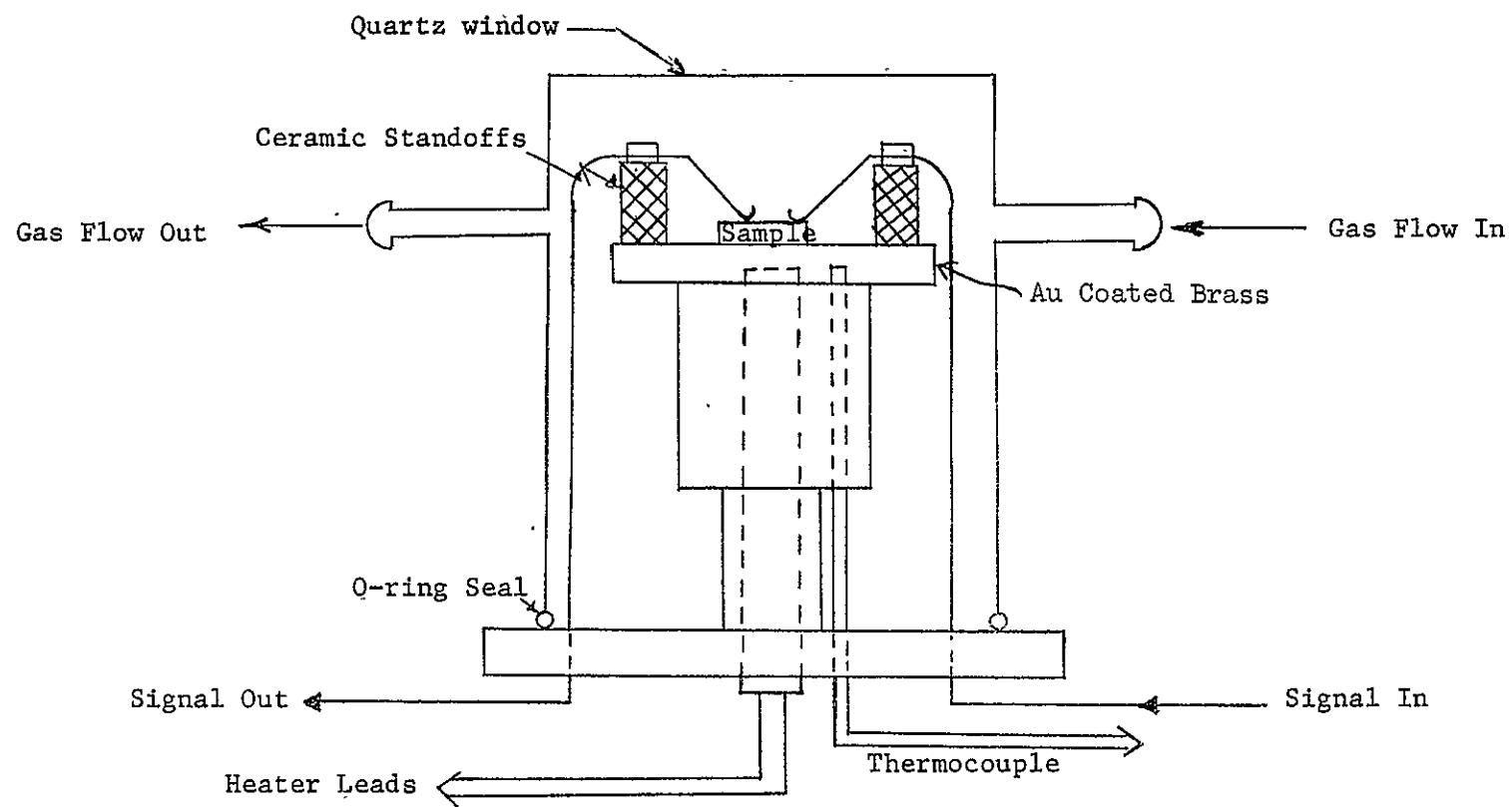


Figure 2.5. Test Envelope

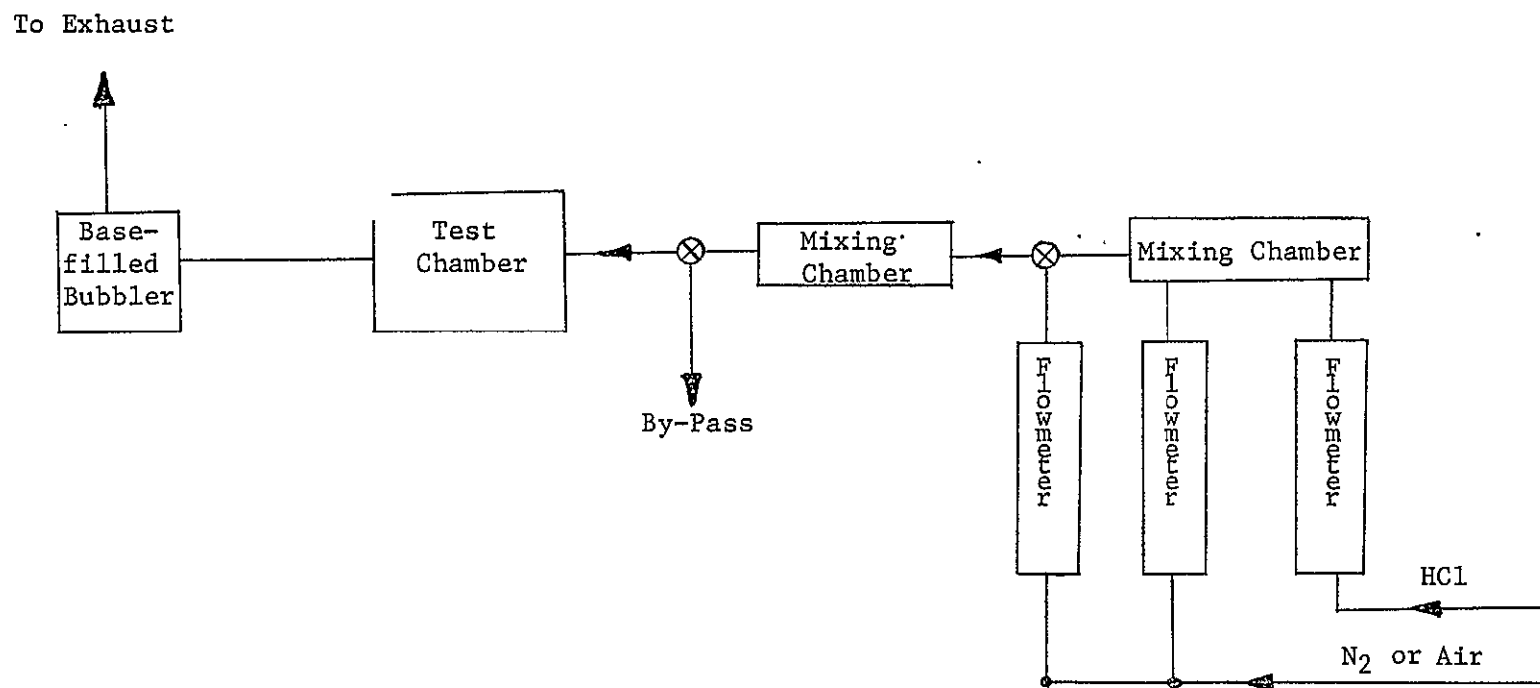


Figure 2.4. Gas Delivery System

took place entirely in the first bubbler, as there was no evidence of any precipitate in either of the other two bubblers. The  $\text{AgNO}_3$  from the 1st bubbler was worked-up in a manner described by Skoog and West, Analytical Chemistry [2]. Several drops of nitric acid were added, and the solution was heated to near boiling for five minutes and was allowed to stand overnight in a darkened place. The precipitate was filtered, washed, dried ( $\approx 100^\circ\text{C}$  at reduced pressure for two hours), and weighed. From the weight of the recovered  $\text{AgCl}$  and the known length of bubble time, the actual flow rate of  $\text{HCl}$  was determined and the flowmeter indication was correlated to the determined value. This correlation is shown in Fig. 2.6.

A second concern which the  $\text{AgNO}_3$  was useful in alleviating was the question of the length of time required for  $\text{HCl}$  to actually get to the sample. It has been reported that due to absorption of the walls of the gas delivery system, the gas arrival time may be hours. In our work we have not encountered this problem, and by monitoring when precipitation begins to appear in an  $\text{AgNO}_3$  bubbler connected to the system outlet, we have determined "worst-case" times for  $\text{HCl}$  to get to the sample. For the 84 ppm mixture flowing at 0.1 l/m, precipitate was observed in a 12-18 minute time range. But it should be noted that this time is quite obviously a function of flow rate and gas concentration. For example, extrapolation to a flow rate of 0.01 l/min with a concentration of 10 ppm, yields a time lag of up to 24 hours.

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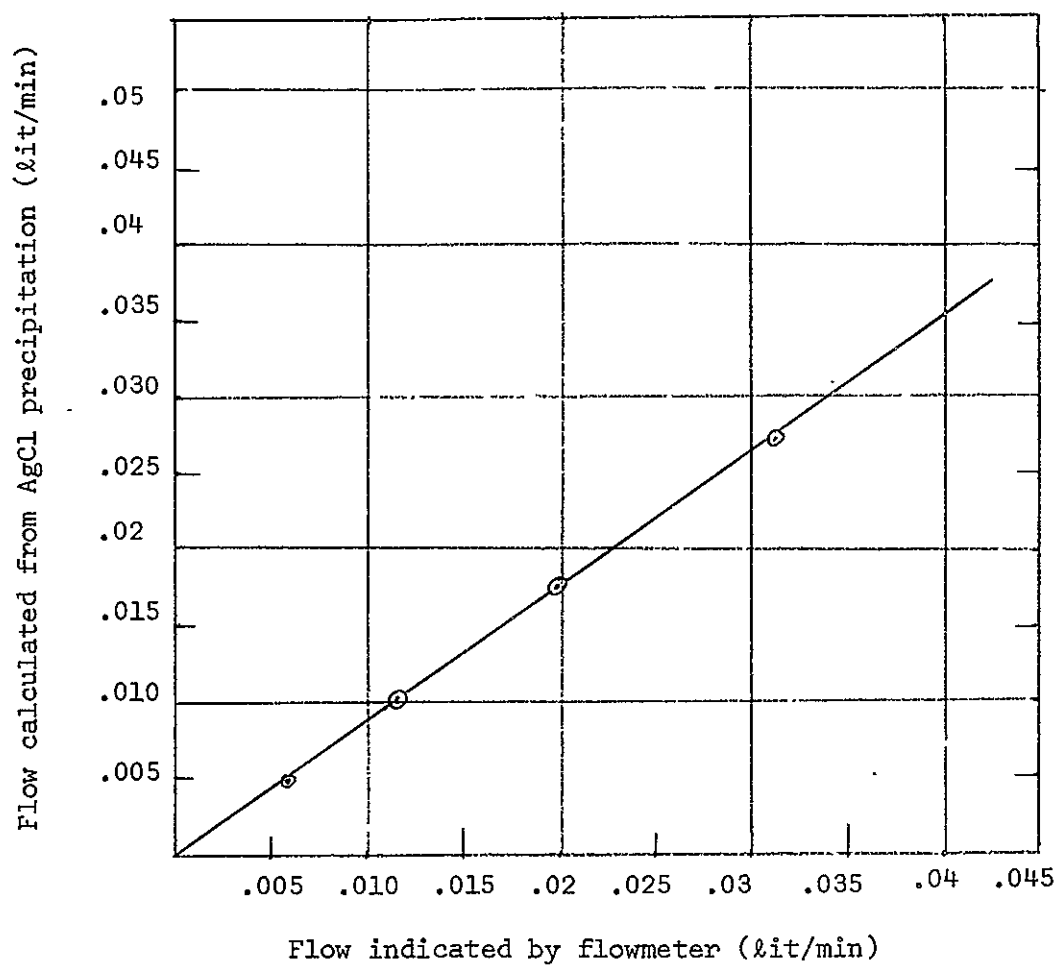


Figure 2.6. Flowmeter calibration for the HCl gas flow.

### 3. Materials Examined

This section deals with the materials which have been examined in the course of the project. Sample preparation is described, along with the nature of the metallic contacts. Reaction or response to HCl is indicated.

#### 3.1 Zinc Oxide (ZnO)

Zinc Oxide was tested in this laboratory as a sensor for oxygen. As a result of that investigation, there was a sputtering target availability. Films were RF sputtered onto Corning #7059 glass substrates, a glass specially prepared for this type work. Films of 3700Å were sputtered at a rate of 7Å/sec; ≈1000Å gold contacts were vacuum deposited onto these sputtered films. These contacts were found to be ohmic, as were aluminum contacts, in the range -20V to +20V. The sample films were annealed at 350°C for 30 minutes, and thicknesses were determined by optical interferometry.

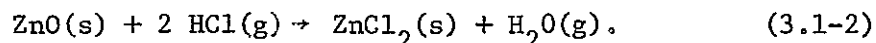
There did appear to be a slight response of these films to high concentrations of HCl. The response of two samples is indicated in Table 3.1-1.

Table 3.1-1. Response of ZnO to HCl

Film Thickness (Å)	$R_o$ (ohm)	$\Delta R$ (ohm)	%change	T(°C)	%HCl
3700	$4.5 \times 10^6$	$+1.2 \times 10^6$	+26.7%	130°	≈50
2700 <sup>a</sup>	$2.3 \times 10^6$	$+1.6 \times 10^6$	+69.6%	160°	≈50

<sup>a</sup> Sample received from H. K. Sarin of this laboratory.

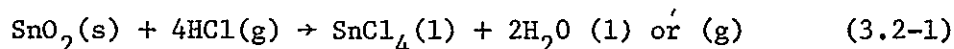
It was noted with both of these films that the resistance value never returned to the pre-exposure value,  $R_o$ , always remaining higher. Because resistance is inversely proportional to the film thickness, it was speculated that the surface of the film was being etched by the HCl gas. This could be accounted for by the following reaction:



The standard free energy change for this reaction ( $\Delta G_f^\circ$ ) is -21.3 kcal/mole (thermodynamic data from Lange's Handbook of Chemistry [3]), indicating a suitable driving force for a spontaneous reaction. To verify that this indeed was occurring, a film surface was photographed before and after exposure to ~20% HCl in N<sub>2</sub> at 230°C. These photographs (see Fig. 3.1) showed significant surface reaction. Also in Fig. 3.1 is a photograph of a second sample from the same sputtering 'run' exposed to the same HCl concentration at a temperature of 300°C; it reveals more intense reaction and surface damage and some deterioration of the aluminum contact. Because of the surface reaction and relatively small resistance change to such a large HCl exposure (see Table 3.1), ZnO was abandoned.

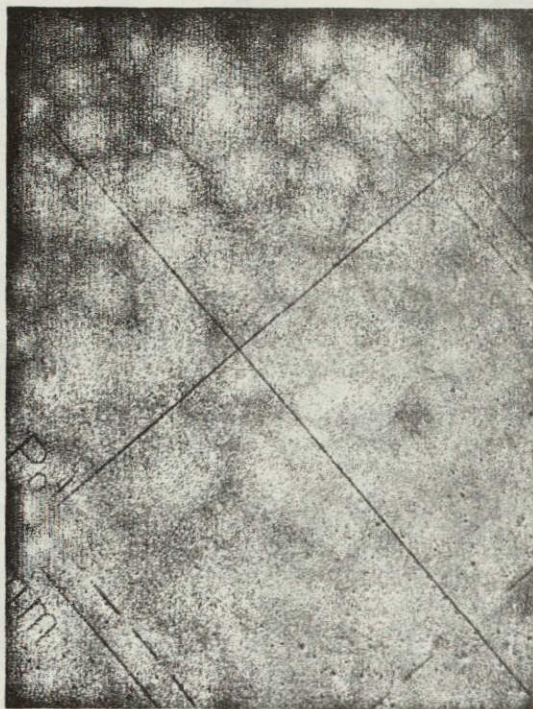
### 3.2 Tin Oxide (SnO<sub>2</sub>)

Because the ZnO has responded to the HCl, the possibility of finding another oxide with a larger response to HCl seemed an appropriate course to follow. To that end SnO<sub>2</sub> was investigated. Because Sn shows a tendency to form tetravalent halides [4], the following reaction could be postulated which might give surface deterioration:

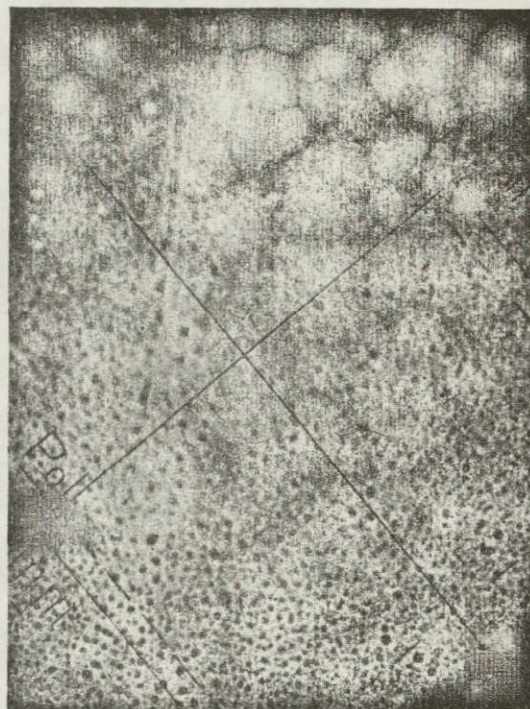


The  $\Delta G_f^\circ$  for the reaction depends on the temperature and whether water or water vapor is formed, giving -3.3 kcal/mole or +0.8 kcal/mole, respectively. The entropy term for this reaction is relatively large due to the randomization of the liquid and gaseous reaction products; this indicates that temperature modulation should be exercised.

Films of 3500 Å thickness were prepared by RF sputtering with an argon plasma. Aluminum contacts ( $\approx 1000\text{\AA}$ ) were vacuum deposited. These contacts were found to be non-ohmic near zero dc bias but were linear from the range of 8-20 volts (dc). Therefore, a 16 volt bias was applied to the



a)



b)

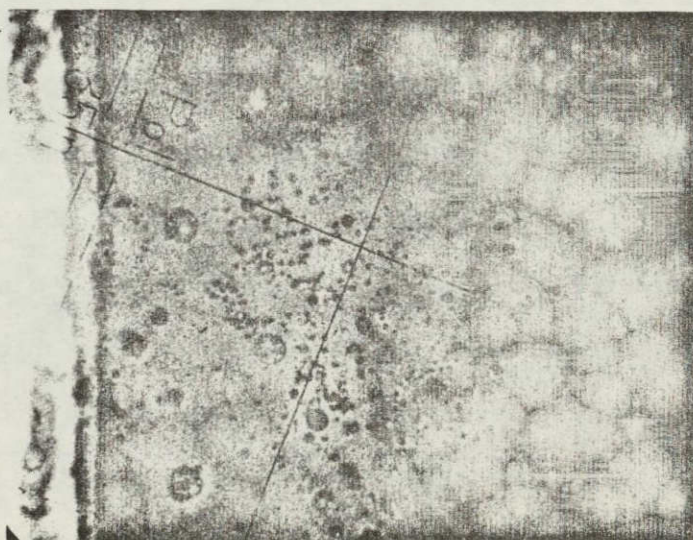


Figure 3.1. The effect on ZnO films to brief exposures to 10% HCl in  $N_2$  concentration at 230°C and 300°C. (a) before HCl exposure, (b) after HCl exposure at 230°C and (c) after HCl exposure at 300°C.

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samples considered. Initially, it was decided to check for surface reaction in the 100°C-200°C temperature range. The initial exposure at 150°C to ~10% HCl in N<sub>2</sub> yielded a significant response. Repeated exposure yielded smaller and smaller responses and deviation of the resistance from the pre-exposure value was again noted. This was repeated with a second sample under the same conditions. Microscopic examination again shows extensive surface reaction. A third sample was exposed briefly to ~1% HCl at 200°C and resulted in significant surface damage. Finally a sample was exposed at 350°C to 1% HCl, with the SnO<sub>2</sub> disappearing almost immediately, presumably via equation (3.2-1), with the SnCl<sub>4</sub> boiling off (bp = 113°C). This concluded the SnO<sub>2</sub> investigation.

### 3.3 Cadmium Sulfide (CdS)

As an alternative to the metal oxides of previous investigations CdS was examined although the following reaction



has a  $\Delta G_f^\circ$  of -7.7 kcal/mole. Films of ~2100 Å were RF sputtered and 1000 Å indium contacts were vacuum deposited. These contacts proved to be ohmic.

A sample was brought to equilibrium at 140°C and indicated an R<sub>0</sub> value of 1.7x10<sup>8</sup> ohms. This sample was exposed to 10% HCl and the resistance increased to 2.2x10<sup>8</sup> Ω ( $\frac{\Delta R}{R_0} \times 100 = 30\%$ ) in 45 minutes. After exposure the resistance returned to ~2.0x10<sup>+8</sup> ohms. In an effort to photodesorb (films are photosensitive) any remaining HCl, the film was illuminated with a tungsten-iodide lamp. After illumination the dark resistance was still ~2x10<sup>8</sup>. Microscopic examination showed surface etching.

A 500 Å sample (R.F. sputtered) was secured from Mr. J. T. Oakes of this laboratory to examine the response of thinner films.



Exposure to 10% HCl at 140°C caused an increase of ~60% in the  $R_0$  pre-exposure resistance value of  $7 \times 10^8$  ohms. Microscopic examination showed severe etching of the film on contact and is the probable explanation for the films failure to decrease from the higher resistance value after the HCl was removed (See Fig. 3.3-1). Because of the surface reaction and the length of time involved in absorption (greater than 1 hr.) CdS was abandoned.

### 3.4 Silver Halides

It has been the experience in this laboratory that ZnO responded to oxygen and CdS responded to  $SO_2$ . By using these cases as examples, it was decided to investigate the metallic halides. In particular, silver halides were chosen as the initial material of investigation due to their insolubility in water and the extensive research devoted to characterizing their electrical and chemical properties (owing to importance of photographic industry).

#### 3.4.1. Silver Chloride (AgCl)

The work with AgCl can really be divided into two phases — early attempts to make dc measurements and later ac measurements.

##### 3.4.1a. Film Preparation and Study Using DC Measurements

Initially the films were to be prepared by both RF sputtering and vacuum evaporation. However, a problem was encountered with the sputtering target. It appeared that the AgCl target did not adhere well to the support plate (the AgCl target is connected to the support plate with a heat-conducting silver epoxy), and it had to be returned to the manufacturer twice for re-bonding. When the target was returned, the target again separated at sputtering powers of 50 watts or less. Therefore, with the supplier seemingly unable to solve this bonding problem, the bulk of the AgCl films were prepared by evaporation. Gold contacts were used as they had been reported to be ohmic by Baetzold [5], and this was verified.

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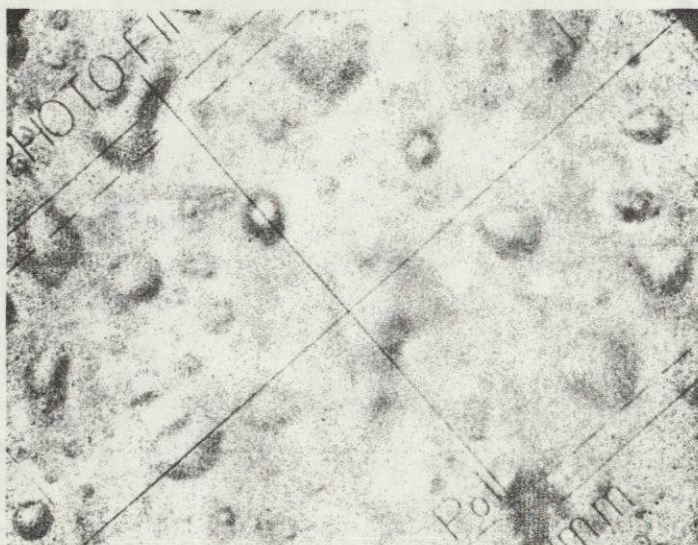


Figure 3.3-1. Surface damage to 500 Å CdS film after exposure to 10% HCl in N<sub>2</sub> at 140°C.



Some films prepared by RF sputtering onto Corning #7059 glass substrates appeared to be silver rich (evolution of chlorine during the sputtering process), being purple-ish in color and only partially transparent. Baetzold[5] has reported that the films do not become continuous until they are close to 1000 Å. In accord with this observation, 850 Å films (thickness determined by optical interferometry) were prepared and studied. The film-contact geometry used on all samples in this study is shown in Fig. 3.4-1.

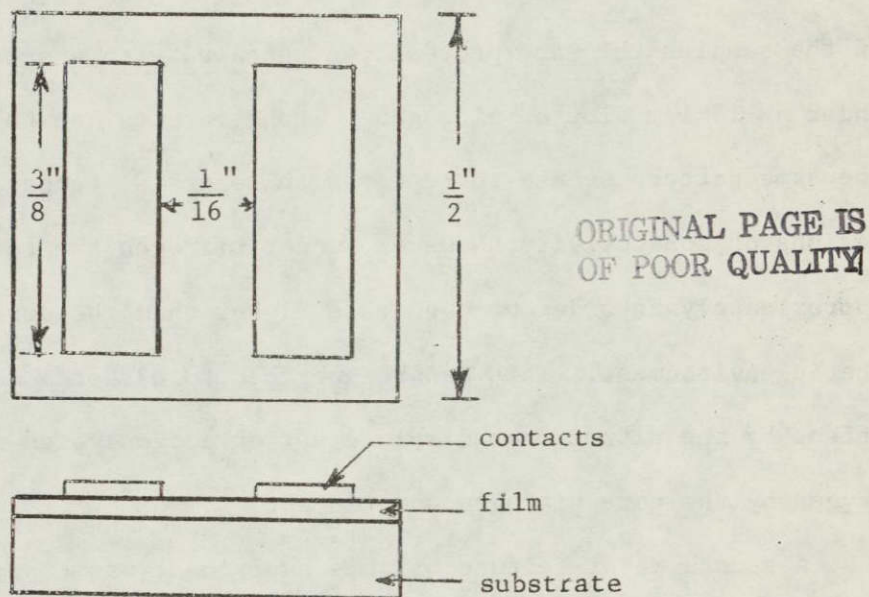


Figure 3.4-1. Sample Geometry

Silver Chloride is different from the materials previously reported in sections 3.1 through 3.3 because the conductivity is ionic in nature with the positive ion being the mobile species[6]. The conductivity ( $\sigma$ ) should be a function of temperature ( $T$ ) of the form.

$$\sigma = \sigma_0 e^{-E_a/kT} \quad (3.4-1)$$

where  $E_a$  is the activation energy and  $k$  is Boltzmann's constant. In order to characterize this temperature — resistivity (reciprocal of conductivity) relationship, one of the 850 Å films was heated in 25°C



increments in the atmosphere with a +20 bias applied to the samples. The results of this process are shown in Fig. 3.4-2. The important feature of this graph is the very sharp kink in the curve. This indicates two mechanisms of conductivity, one at low temperatures and one at higher temperatures, with the break point occurring at about 112°C. This is the same type behavior reported by Mott and Gurney [6] and Lehfeldt [7], and these conductivity values are almost equal in magnitude to the values which they reported.

In order to determine if atmospheric oxygen influences the conductivity of the samples the same process was repeated with a second 850 Å sample under a .15 l/m flow of nitrogen. These results are shown in Fig. 3.4-3. The same pattern seemed to repeat with separate, temperature-dependent regions of conductivity; however, under nitrogen the resistivities are approximately an order of magnitude higher than the corresponding atmospheric environment. This can be ascribed to either a depletive surface effect by the nitrogen or displacement of accumulation inducing surface oxygen by the pure nitrogen environment.

A second major feature of this experiment was that, on cooling, the resistivity remained over an order of magnitude higher than it had been prior to heating. This led to the microscopic examination of these samples, and revealed structures extending from the cathode electrode of both of these films (See Fig. 3.4-4). Mott and Gurney [6] have reported that AgCl when subjected to dc potentials will form random dendritic structures of Ag, through the following cathodic reaction



This did appear to be the case, as qualitatively the effect did not seem nearly as severe at lower film bias potentials. If the ionic mobility is assumed to remain constant, an interesting situation develops. On

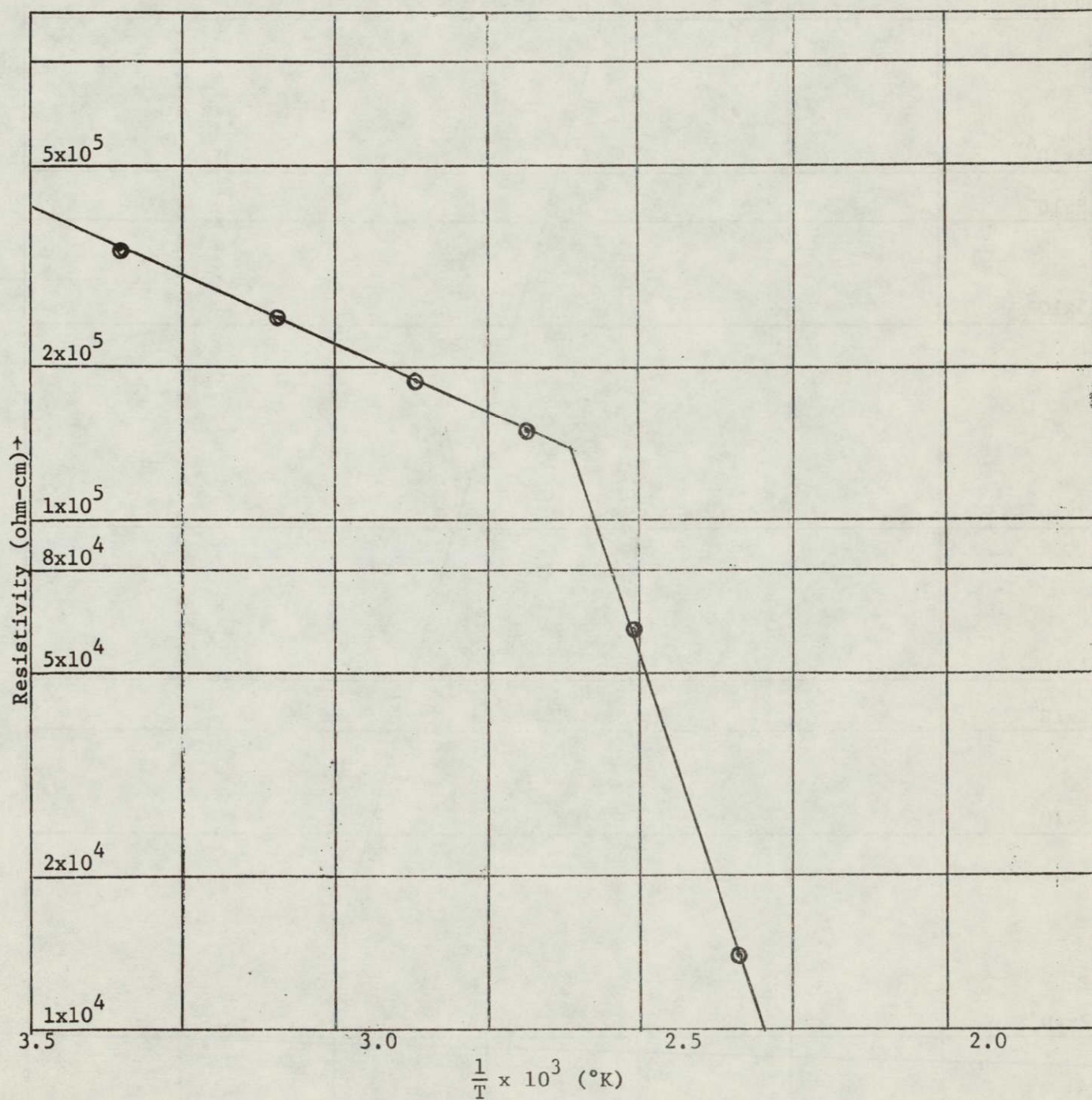


Figure 3.4-2. Resistivity of 850Å AgCl film vs. temperature in atmosphere with 20 volt dc bias.



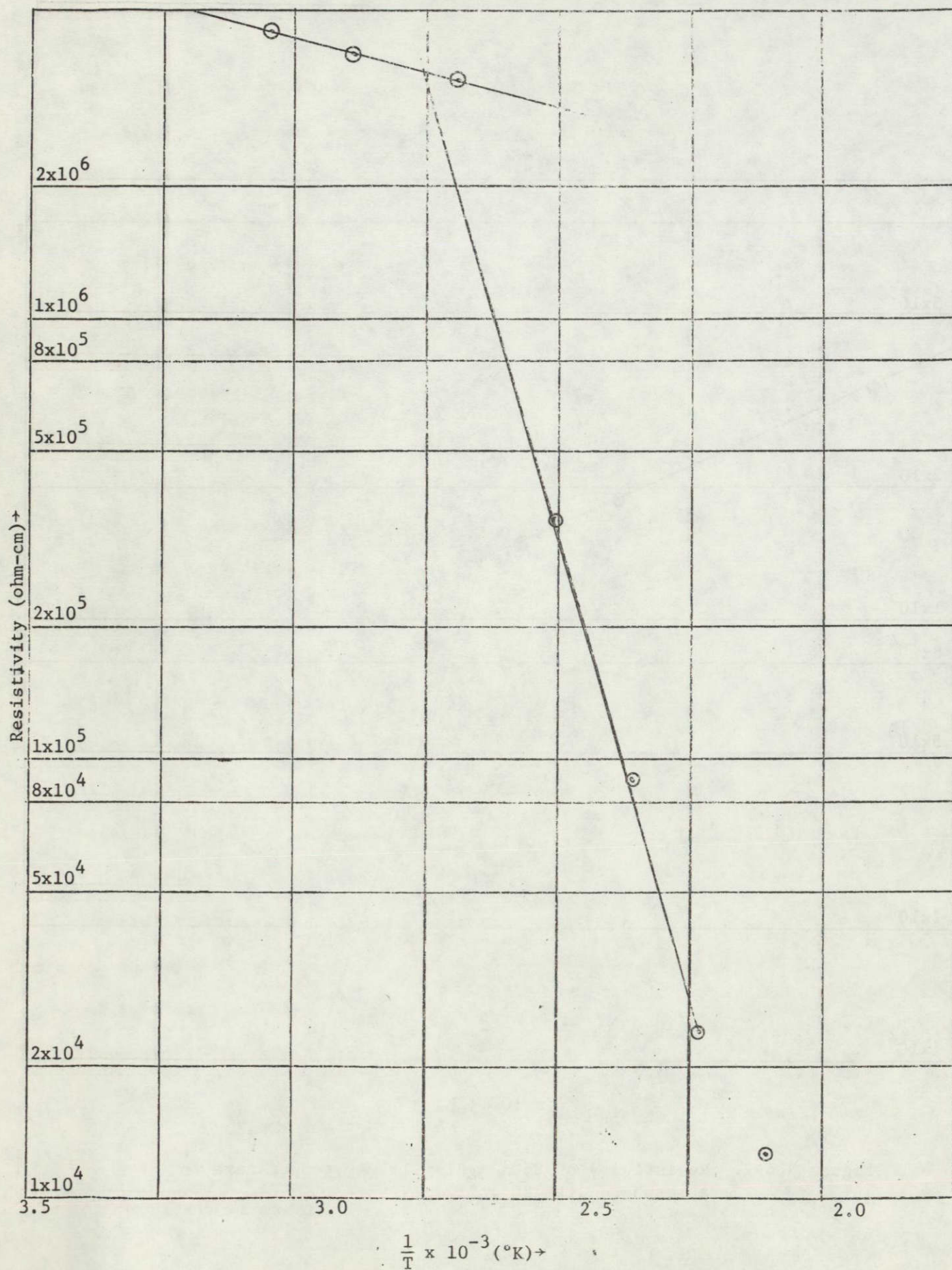


Figure 3.4-3. Resistivity vs. temperature of 850Å AgCl film with 20V dc bias under N<sub>2</sub> ambient.

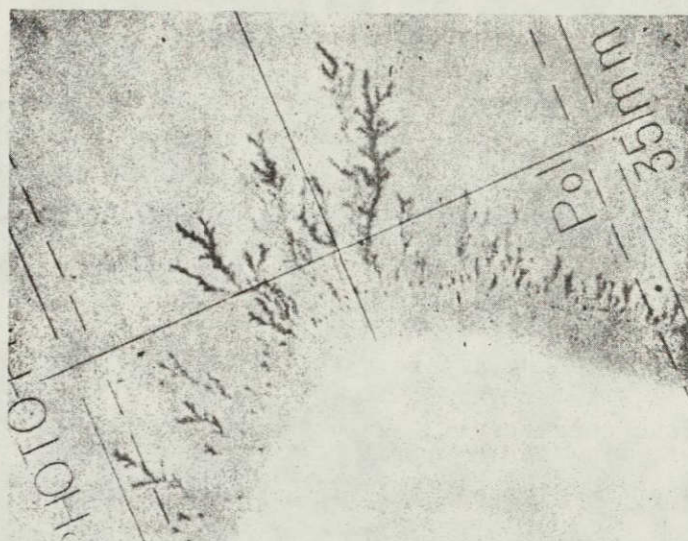


Figure 3.4-4. Example of cathodic dendrite growth on AgCl film with 20V dc bias.

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one hand, the reduction of interstitial charge carriers should be increasing the sample resistance, and on the other, an effective reduction of the contact separation due to the silver dendrites should be decreasing the sample resistance. It appears that the latter trend is dominant with the silver rich sputtered samples. The most important consequence of the dendrite formation is that the reproducibility of data is very difficult.

We determined that we had very good film growth control by vacuum deposition of the AgCl, as opposed to R.F. sputtering. The evaporated films were quite transparent and colorless and thicknesses were reproducible. A set of 850 Å AgCl films was prepared and 1000 Å gold contacts were deposited.

To determine if these films respond to HCl one of the 850 Å films (vacuum deposited) was exposed to concentrations of HCl in N<sub>2</sub> of 1875 ppm to 30000 ppm. Before the HCl was added, the sample resistance was  $1.4 \times 10^{11}$  ohms at 50°C under an N<sub>2</sub> atmosphere. This was about the same value as the 850 Å sputtered film under the same conditions ( $2 \times 10^{11}$  ohm for sputtered film). The results of the HCl exposures are shown in Fig. 3.4-5. A 20 volt bias was applied to the sample. The difficulty in plotting this data is that the  $R_0$  (and therefore  $I$ ) value changed with the changing conductivity value. What is plotted is  $\Delta I/I'_0$ , where  $I'_0$  is the value to which the sample returned from the previous exposure. Thus data is rather scattered, and it cannot be determined to be linear. However, it would appear the absolute lower limit of sensitivity would be about 400 ppm, and more likely, above 1000 ppm.

The randomness of this data point out the need for stable film test conditions which were achieved with the ac measurement system. This need was further amplified by the lack of any consistent patterns in the data collected with the dc system. An example of this inconsistent sample behavior can be seen in Table 3.4-1 where a single sample of the 850 Å

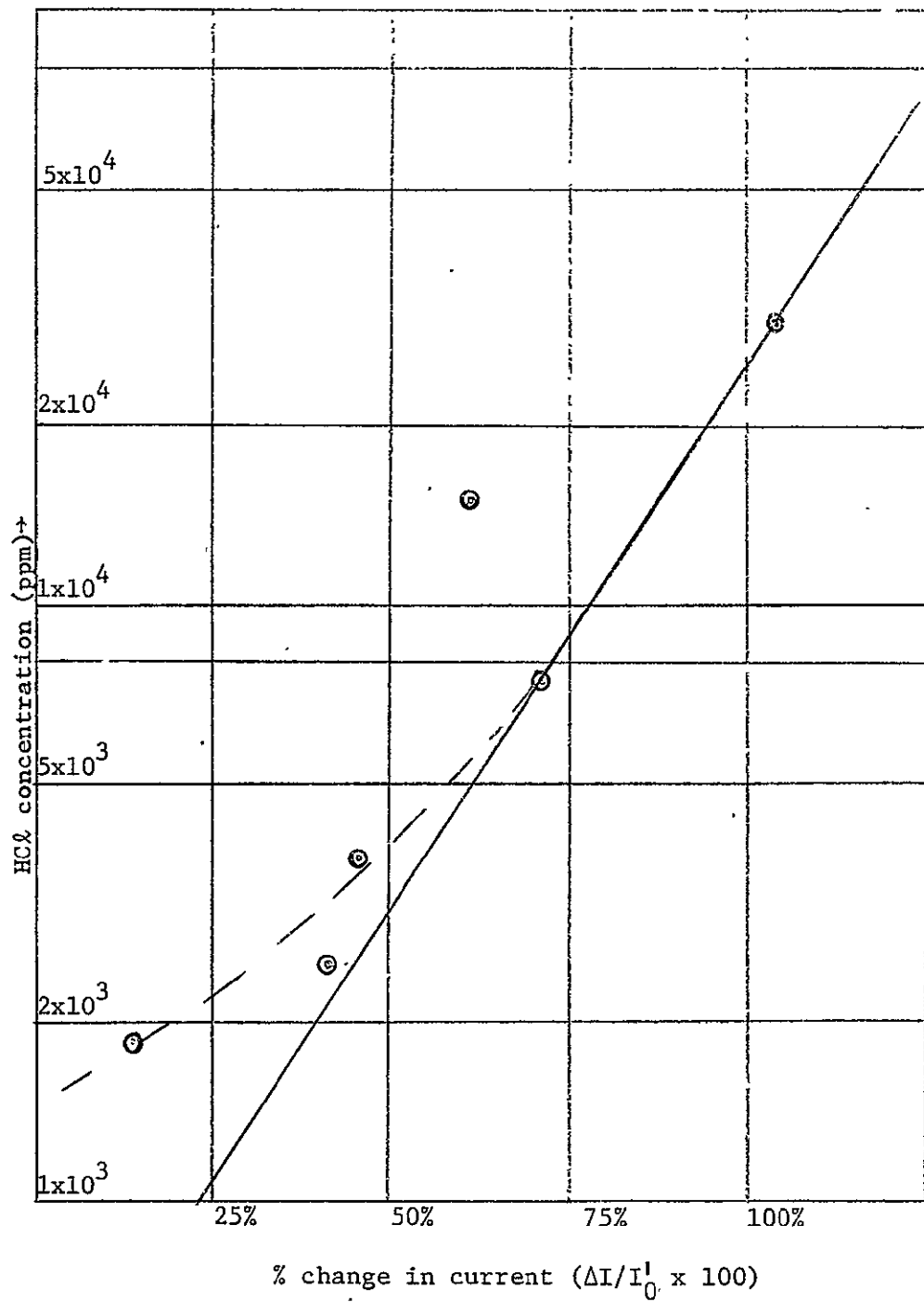


Figure 3.4-5. Exposure of 850 Å AgCl film to HCl at 100°C.

evaporated film was cycled twice between 30,000 ppm and 15000 ppm HCl at a temperature of 150°C. After each exposure the sample temperature was raised to 175°C for 10-15 minutes to desorb as much as possible, and the samples were allowed to come to equilibrium on cooling to 150°C.

Table 3.4-1. Two Cycles of HCl exposure of 850 Å sample at T=150°C.  
A cycle consists of exposure to 1.5% thru 3.0%.

Exposure	$I'_0$ (A)	T(°C)	$\Delta I/I'_0 \times 100$	%HCL	
1	$4.6 \times 10^{-9}$	150°	13%	1.5%	cycle #1
2	$5.8 \times 10^{-9}$	150°	19%	3.0%	
3	$1.0 \times 10^{-8}$	150°	20%	1.5%	cycle #2
4	$2.0 \times 10^{-8}$	150°	15%	3.0%	

Studies on a thinner sample of AgCl were also conducted. Films of  $\approx 400$  Å were deposited, and 1000 Å gold contacts were placed on the film. These films were brought to equilibrium under a constant 0.3 l/m flow of nitrogen. The exposure data is shown in Table 3.4-2.

Table 3.4-2. Exposure data for 400 Å AgCl films at room temperature.

%HCL	$I'_0$ (A)	$\Delta I/I'_0 \times 100$	
1%	$8.5 \times 10^{-9}$	276%	cycle #1
15%	$8.5 \times 10^{-9}$	9300%	
1%	$4.3 \times 10^{-9}$	30%	cycle #2
6%	$4.3 \times 10^{-9}$	1700%	
3%	$4.5 \times 10^{-9}$	1122%	cycle #3

Again there does not appear to be a clear pattern to the data; it is important that the magnitude of the current change is much greater than for the case of the 850 Å films.

It became more and more evident that the problems with non-predictability and reproducibility of the samples response using dc techniques could not be readily solved. However, several important features were recovered from the dc work.

1. In going from atmospheric environment to pure  $N_2$ , the film resistance rose at least an order of magnitude.
2. Contrary to the data of Baetzold [5], we did appear to have conductive films at 400 Å. This laid the groundwork for very thin films.
3. The sensitivity limit for the 850 Å films was  $\approx 400$  ppm.
4. The sensitivity of 400 Å films was much greater than the 850 Å films. To switch to the ac measurement system of Fig. 2.2-1 proved quite easy; the ac work will be described in the next section.

### 3.4.1b. AC Measurement Work

As had been the case with dc measurement the initial aim was to characterize the conductivity (or resistivity) of the sample films. A set of films was carefully prepared by vacuum evaporation. These films had thicknesses of 1100 Å, 2200 Å, 3300 Å, and 4400 Å. Gold contacts (1000 Å) were deposited. Half of the samples of each thickness were annealed in vacuo at 120°C for 30 minutes and the other half were not.

Since resistance has the same functional form as resistivity

$$R = R_0 e^{E_a/kT} \quad (3.4-3)$$

it can be seen that the plot of the logarithm of  $R$  vs.  $1/kT$  is theoretically a straight line with slope equal to the activation energy. In order to eliminate surface effects, these resistances were measured in a vacuum. Figure 3.4-6 shows the variation of resistance with temperature for the unannealed 3300 Å AgCl film. Similar variation in resistance with temperature was obtained for films of other thicknesses. The values of activation energy  $E_a$  and  $R_0$  for these films are shown in Table 3.4-3. The values of  $E_a$  in Table 3.4-3 are somewhat lower than the values given by Baetzold [5]. Baetzold's values ranged from 0.33 eV to 0.66 eV and were dependent on the substrate used.



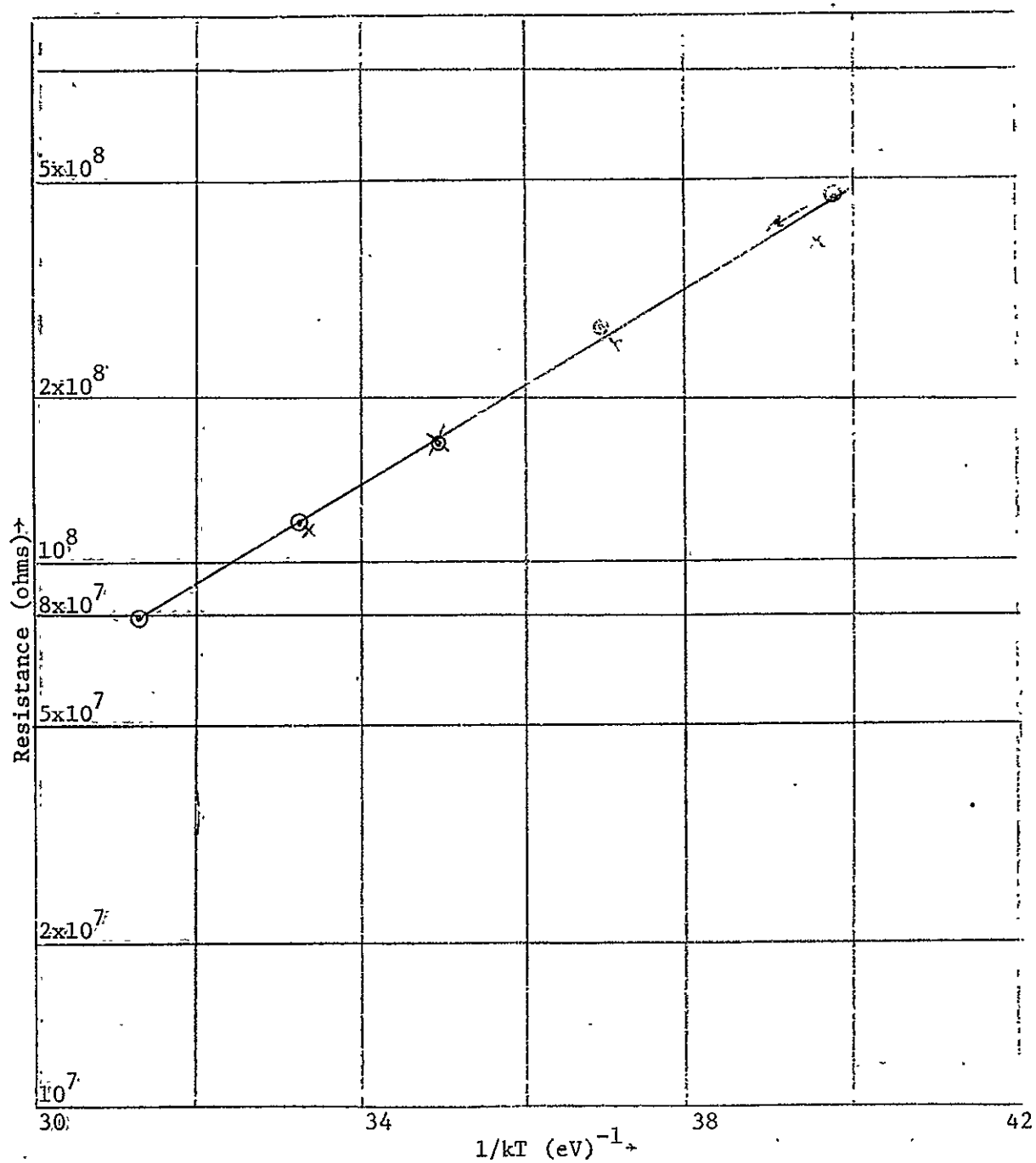


Figure 3.4-6. Resistance vs. temperature in vacuum for unannealed 3300A evaporated AgCl film. o - heating cycle: room temp. to  $100^\circ\text{C}$ ; x - cooling cycle:  $100^\circ\text{C}$  to room temp.

Table 3.4-3. Results of  $R_o$  and  $E_a$  measurements

Film Thickness ( $\text{\AA}$ )	$E_a$ (eV)	$R_o$ (ohm)
1100 - Unannealed	0.27	$5.2 \times 10^4$
1100 - Annealed	0.27	$6.8 \times 10^4$
2200 - Unannealed	0.24	$7.8 \times 10^4$
2200 - Annealed	0.21	$3.0 \times 10^5$
3300 - Unannealed	0.20	$1.3 \times 10^5$
3300 - Annealed	0.28	$7.5 \times 10^4$
4400 - Unannealed	0.22	$7.0 \times 10^4$
4400 - Annealed	0.23	$7.0 \times 10^4$
Average values	0.24	$1.05 \times 10^5$

Therefore, we feel that these values are not all unreasonable. (Baetzold did not use glass substrates). These films were quite stable for long periods of time in the vacuum at room temperature, but did show a slight decrease in resistance (about 5% per 12 hrs.) if stored at  $80^\circ$ - $100^\circ\text{C}$  under reduced pressure. Whether this is a temperature effect, pressure effect, or simply aging of the film has not been determined. This mild drift in film resistance was also noted for samples heated for a long time under nitrogen.

The next step was to expose films to HCl. Three fresh sets of 2200  $\text{\AA}$ , 700  $\text{\AA}$  and 300  $\text{\AA}$  films were deposited, and contacts were placed on them in the usual fashion. The frequency of the test system was set at 1.6 Hz, and the reference voltage was set at 0.7 volts rms. The exposure data of these films are shown in Table 3.4-4.

The 300  $\text{\AA}$  films had very high resistances and apparently the exposure to 84 ppm caused the resistance values to exceed thus increasing the noise level of the sample above the noise level of the measuring system. The signal from two separate films became very erratic when exposed, and the temperature had to be kept at  $400^\circ\text{K}$  to get measurable signals.

Table 3.4-4. Exposure data for (a) 2200 Å AgCl films, (b) 700 Å AgCl films, and (c) 300 Å AgCl film (HCl in N<sub>2</sub> ambient)

(a) 2200 Å					
T	N <sub>2</sub>	HCl	V <sub>1</sub>	ΔV <sub>1</sub>	ΔV/V <sub>1</sub> × 100
300°K	0.3 l/m	.006 l/m (2%)	3 mV	-0.5 mV	16%
335°K	0.3	.051 (15%)	10.5 mV	-10.4 mV	99%
340°K	0.3	.014 (4%)	10 mV	-7.5 mV	75%
350°K	0.3	.008 (2.5%)	4.4 mV	-2.8 mV	64%
350°K	0.3	.008 (2.5%)	4.4	-2.7 mV	61%
383°K	0.3	.009 (2.9%)	90	-20 mV	22%
420°K	0.3	.013 (4%)	390	no measurable change	
420°K	0.3	.05 (15%)	390		
338°K	0.3	.003 (1%)	4.0	-0.95 mV	23%
(b) 700 Å					
T	N <sub>2</sub>	HCl	V <sub>1</sub>	ΔV <sub>1</sub>	ΔV <sub>1</sub> /V <sub>1</sub> × 100
400°K		84 ppm	140 mV	no meas. change	
400°K	0.8 l/m	.003 (.37%)	140	< 1 mV	-
400°K	0.8	.008 (1%)	137	- 3 mV	2.1%
400°K	0.8	.016 (2%)	134	- 7 mV	5%
400°K	0.8	.032 (4%)	140	-10 mV	7%
400°K	0.3	.03 (10%)	133	-53 mV	39%
(c) 300 Å					
T	N <sub>2</sub>	HCl	V <sub>1</sub>		
400°K	-	84 ppm (.15 l/m)	.04 mV	measured signal became very erratic when HCl introduced.	
420°K	-	84 ppm (.15 l/m)	.06		

The 700 Å films showed a very slight response to 3700 ppm, but almost too small to be reliably measured by detecting less than 1 mV in 140 mV.

The 2700 Å films yield some useful information. It appears that there is an optimum temperature in the range of 350°K. This was determined from the following:

1. At 300°K 2% HCl produces a 16% change in the measured voltage.

2. At 350°K 2.5% HCl produces a 60-65% change in the measured voltage.
3. At 383°K 2.9% HCl produces only a 22% change.
4. At 338°K 1% HCl produces a 23% change.

However at this temperature (350°K) there is a real problem because a film of hydrochloric acid (HCl dissolved in atmospheric moisture) can form on the sample and retard any further response, with the system measuring the conductivity of the acid, as opposed to the sample. The magnitude response for the 700 Å films was much less than for the 2200 Å films which was contrary to the case seen in dc measurements where thinner films gave greater responses. This has been attributed to the temperature (400°K) at which those films were operated to avoid the acid coating problem. The very significant implication is that the response varies inversely with temperature above the optimum region. This seems to exclude the chemisorption mechanism. Generally, chemisorption has an activation energy requirement and is enhanced by temperature.

Even with the ac measurement the response of very thin films (less than 400 Å) was erratic since the noise from the sample exposed to HCl exceeded the noise level of the measurement system. Electrically active impurities added to the film reduced the resistivity, hence the sample noise. The doping of AgCl with cadmium chloride ( $\text{CdCl}_2$ ) to produce additional interstitial  $\text{Ag}^+$  has been known for a long time and is described in literature [8].

The doping method used was similar to that of Baetzold [5]. Various thicknesses of  $\text{CdCl}_2$  were vacuum evaporated onto freshly cleaned substrates. On this layer was deposited various thicknesses of AgCl, and finally, gold contacts were added. The samples were then annealed at 150° for 30 minutes. Baetzold reported that Auger analysis of samples prepared by this technique showed no segregation of impurities [5].

A matrix of films was prepared, with thicknesses being determined by a Sloan Deposition Monitor on the vacuum evaporation system. Films of  $\text{CdCl}_2$  of 25 Å, 70 Å, and 250 Å were prepared. On these films, AgCl of 100 Å, 400 Å, 800 Å and 1500 Å thickness was deposited. Gold contacts of ~1000 Å were then added, and the samples were annealed.

In order to expedite the investigation of these samples, the four AgCl thicknesses of a single  $\text{CdCl}_2$  thickness were exposed to 30% HCl in  $\text{N}_2$ . For the one which yielded the greatest response, the other  $\text{CdCl}_2$  thicknesses would be examined. In this manner, nine samples could be eliminated. The thickest  $\text{CdCl}_2$  layer was chosen. The results of the exposures are shown in Table 3.4-5.

Table 3.4-5. Response of AgCl films (doped with 250 Å  $\text{CdCl}_2$ ) to 30% HCl at 400°K

AgCl Thickness	$R_o$	$V_1$	$\Delta R/R_o$
1500	20.2 MΩ	18.5 mV	~2
800	44.5 MΩ	9 mV	7.9%
400	500 MΩ	.8 mV	170%
100	-	-	-

The resistance of the 100 Å films was too great for the system to measure and it is assumed that the film was not continuous. The 400 Å film may not be completely continuous because there is a 10-fold increase in resistance for a halving of the thickness. This data clearly indicates that the best films for study were the 400 Å films, and the other thicknesses were discarded.

The sample with the thinnest  $\text{CdCl}_2$  layer showed a resistance much higher than the other two thicknesses. Therefore, it too, was discarded. The results of exposures of the two remaining films are shown in Table 3.4-6.

Table 3.4-6. Exposure data for (a) 400 Å AgCl film doped with 250 Å CdCl<sub>2</sub>, (b) 400 Å AgCl film doped with 70 Å CdCl<sub>2</sub> at 400°K.

a)	$V_1$ (mV)	$\Delta V_1$ (mV)	T (°K)	HCl in N <sub>2</sub>	$\Delta V_1/V_1 \times 100$
	0.88	-0.05	400	35 ppm	5.6%
	0.79	-0.04	400	35 ppm	5.0%
	0.61	-0.19	395	0.3%	31%
	0.62	-0.10	398	3%	16%
	0.86	-0.05	400	3%	5.8%
	0.96	-0.04	400	6%	4.1%
b)	$V_1$ (mV)	$\Delta V_1$ (mV)	T (°K)	HCl in N <sub>2</sub>	$\Delta V_1/V_1 \times 100$
	18.0	0.9	398	35 ppm	5%
	11.6	-1.2	395	0.3%	10%
	12.8	1.2	397	3%	9.3%
	10.9	-.8	396	3%	7.3%
	9.7	-.5	397	6%	5.1%

In Table 3.4-6 the larger value of  $V_1$  for the films doped with 70 Å of CdCl<sub>2</sub> suggests that the resistance of these films was approximately 20 times lower than those doped with 250 Å of CdCl<sub>2</sub>. This is an apparent contradiction if one assumes that all the CdCl<sub>2</sub> simply results in electrically active impurities. In addition, there appears to be an aging effect in which repeated exposure of the films seems to decrease the sensitivity. This is shown by the smaller response of both films to 6% HCl, than 3%; also, repeated exposure of the same concentration yielded small responses.

#### 3.4.2. Silver Bromide (AgBr)

Samples of AgBr were prepared by vacuum evaporation. These films were 700 Å thick and had gold contacts placed on them. Exposure to 5% HCl in N<sub>2</sub> showed no response. No further work was done with AgBr.

#### 4. FEASIBILITY OF INSTRUMENTATION

Based on the results of the work on AgCl films, it is felt that HCl sensing with these films is possible but several requirements must be realized. The important parameters which must be considered are (1) temperature, (2) voltage supply, (3) signal to noise restrictions, (4) sampled gas flow rate, (5) absorption-desorption time constant, and (6) responsivity.

##### 4.1 Temperature

The temperature of sensor film (assuming it to be AgCl) must be maintained to within  $\pm 0.5^{\circ}\text{C}$ . This figure can be seen by examining the data of Table 3.4-6, in particular, the first two entries under Part b. It is seen that a  $3\text{ K}^{\circ}$  temperature change ( $398^{\circ}\text{K}$  to  $395^{\circ}\text{K}$ ) produces a change in  $V_1$  of  $\approx 6\text{mV}$ . The  $V_1$  values are about  $1\text{ mV}$  for HCl exposure; therefore, the maximum  $\Delta T$  has to be such that the  $\Delta V_1$  caused by  $\Delta T$  must be less than  $\Delta V_1$  caused by HCl exposure. From this the value of  $\pm 0.5^{\circ}\text{C}$  is derived. Temperature control is very plausible for a laboratory prototype but could present problems for a field instrument.

##### 4.2 Power Supply

The voltage supply would probably be a battery system. Again, since the  $\Delta V_1$  values range from  $40\text{ }\mu\text{V}$  to  $100\text{ }\mu\text{V}$ , the regulation should be such the power supply variations are no more than one-tenth of the low value, or  $4\text{ }\mu\text{V}$ . It would be very difficult to smooth any rectified signal that much. Therefore, it seems that a battery supply would be required.

#### 4.3 Signal to Noise Ratio

Noise considerations pose limitation on both the films and the measuring system, as both are capable of producing noise. In the present research the noise of the measuring system was found to be the limiting factor for most of the AgCl samples. The open circuit voltage was about 1  $\mu$ V with no sample in the system. By considering Johnson noise associated with resistance or

$$V = \sqrt{4kTR\Delta f} \quad (4.1)$$

where  $k$  is Boltzmann's constant,  $T$  is absolute temperature,  $R$  is sample resistance, and  $\Delta f$  is the bandwidth of the lock-in amp, ( $\Delta f = \frac{1}{8 \times \text{time const.}}$  with the time constant usually set at 1 sec.), the sample resistance can be calculated which will yield a noise voltage equal to the system noise level. Therefore,

$$\begin{aligned} R &= \frac{(1 \times 10^{-6})^2}{4(400^\circ\text{K})(.125)(1.38 \times 10^{-23} \text{ Joule}/^\circ\text{K})} \\ &= 0.36 \times 10^9 \text{ ohms} \end{aligned}$$

This indicates that in order to have a reliable, measurable signal, limited by system noise to 1  $\mu$ V or greater but not limited by noise from the thin film sample, the resistance of the film must be 36 megohms or less. The AgCl films must be doped in order to achieve these resistance levels. As it turns out this is one of the major problems encountered in the early course of research which was not fully understood until the doping experiments were completed.

#### 4.4 Sampled Gas Flow Rate

The flow rate of the gas into the measuring instrument should be considered as it may affect response. However, the gas flow rate did not appreciably affect the response with AgCl films except that high flow rates make temperature control more difficult.



#### 4.5 Response Time

Since the AgCl must be used with an ac signal to prevent the cathodic reaction noted previously, it is recommended that the battery voltage be chopped and fed to the sensor, and it is suggested that the necessary instrumentation be a lock-in type amplifier. The time constant of the lock-in amplifier must be shorter than the rise time of the sample being exposed. This presents no problem. A plot of rise time vs. HCl concentration is shown in Fig. 4.1. The time constant of the lock-in amplifier could easily be 30 sec. with film response times of 5 minutes. It is seen that the response time increases with concentration increases for low concentration regions between 10 and 30 ppm. However, the response is fairly constant between 15 and 18 min. for concentrations greater than 100 ppm.

Desorption time was typically longer and did not begin until there had been sufficient HCl desorption from the walls of tubing and the test chamber. For example, the 5000 ppm exposure had a rise time of about 18 minutes and did not begin desorption until 30 minutes after the HCl was removed. The second problem with desorption was the question of complete desorption. The  $V_1$  reading did not fully recover to the pre-exposure value unless the sample was heated briefly (5 min.), at temperatures of 105°C - 170°C. This did seem to drive off any remaining absorbed HCl.

#### 4.6 Responsivity

To determine the sensitivity of the CdCl<sub>2</sub>-doped AgCl films to HCl, low concentration experiments were performed. These were considered essential in determining the feasibility of AgCl as a sensor.

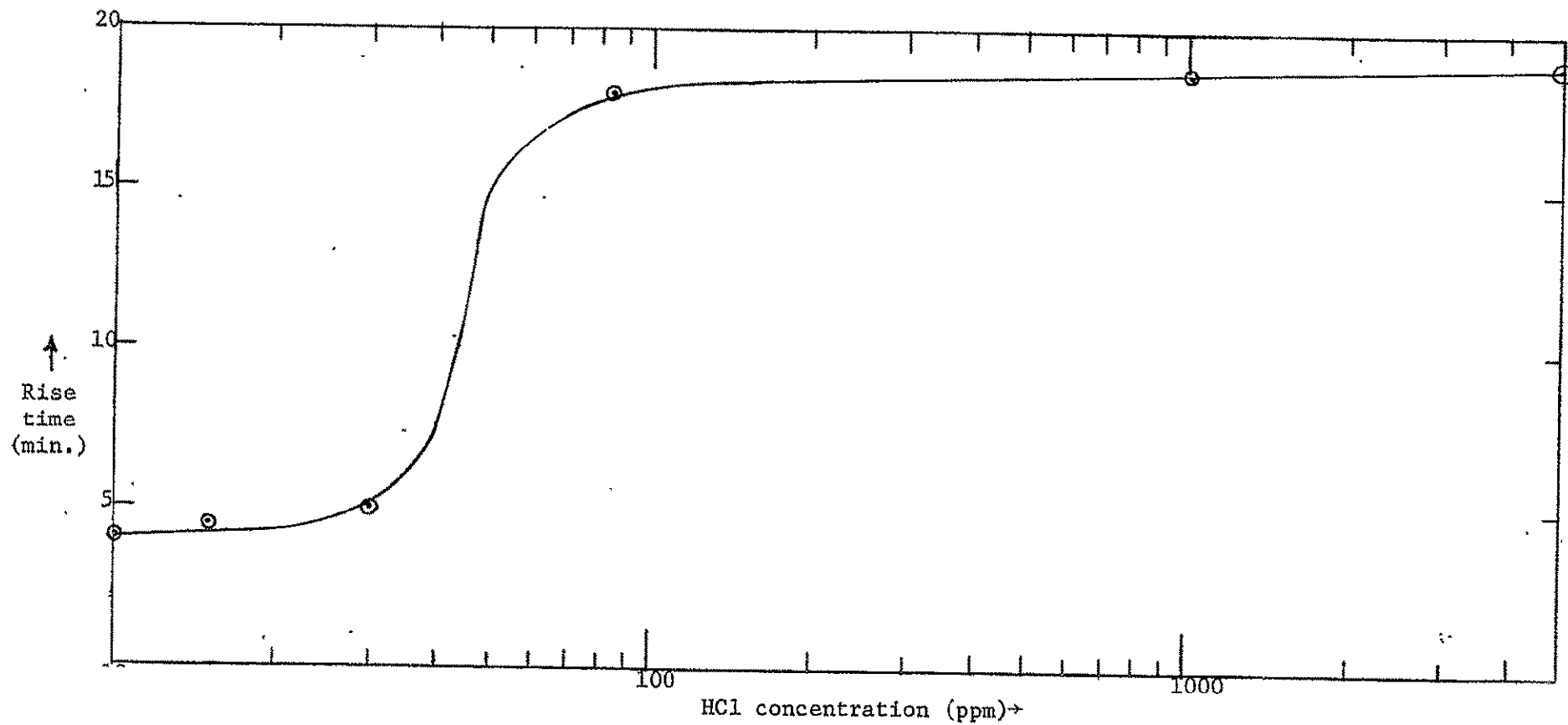


Figure 4.1. Rise time vs. HCl concentration

The films on hand were aged two weeks before this sequence of exposures to try to determine if the aging effect (which had been noted) had a limiting value of desensitization. All the films which had shown a 5% response to 35 ppm HCl showed no detectable response to 84 ppm HCl. Also, the measured voltage,  $V_1$ , which had been 16-18 mV ( $T=400^\circ\text{K}$ ), was 6-8 mV, indicating a two-fold increase in film resistance. A sequence of exposures did produce the following results with one of the films (Table 4-1).

Table 4-1. Exposure Sequence of  $400\text{\AA}$  AgCl,  $70\text{\AA}$  CdCl<sub>2</sub> film.

	$V_1$	$\Delta V_1$	%Change	HCl conc.	(Rise time) Time required
1.	3.0 mV	-.1 mV	3.3%	5000 ppm	8 minutes
2.	3.2 mV	-.3 mV	9.6%	10000 ppm	18 minutes
3.	3.0 mV	-.1 mV	3.3%	5000 ppm	9 minutes

This data indicates that this film, from the same preparation batch as the one which had changed 5% with 84 ppm HCl, is roughly 100 times less sensitive than when freshly prepared and exposed.

To determine if air had any influence on the equilibrium  $V_1$  value, the film, which yielded the data of Table 3.4-8, was exposed to a flow of dry air for 2 days with  $V_1$  rising from 3.35 mV ( $T=113^\circ\text{C}$ ) to 3.4 mV ( $T=113^\circ\text{C}$ ). Therefore, at this operating temperature there did not appear to be much effect on the film on going from nitrogen to air environments. Although no effort was made to quantitatively measure the amount, there did appear to be some change in  $V_1$  in the temperature range of  $250^\circ\text{C} - 300^\circ\text{C}$ . This effect was not measured because the films haven't been operated in this temperature range due to apparent insensitivity to HCl.

The film was next opened to the atmosphere. In doing this it was found that water vapor did not cause drastic changes in  $V_1$  but did cause  $V_1$  to rise from 3.4 to 3.8 mV at  $T=114^\circ\text{C}$ . This seems to agree with the dipole-dipole interaction between the film and gas molecules such as HCl and  $\text{H}_2\text{O}$ , which do have strong dipole moments.

Fresh films of AgCl were prepared ( $\text{AgCl } 400\text{\AA}$ ,  $\text{CdCl}_2 \text{ } 100\text{\AA}$ ). Exposure data is shown in Table 4-2.

Table 4-2. Exposure Data of Fresh  $\text{CdCl}_2$ -doped AgCl Films.

$V_1$	$\Delta V_1$	% Change $\frac{\Delta V_1}{V_1} \times 100$	HCl conc.	Temp.	(Rise Time) Time for Response
16.5mV	-0.7mV	4.7%	84 ppm	402°K	18 min.
16.8mV	-0.4mV	2.8%	30 ppm	403°K	5 min.
16.4mV	-0.3mV	1.8%	20 ppm	402°K	5 min.
2.25mV	-0.05mV	2.2%	15 ppm	366°K	5 min.

At low concentration on the order of 20-30 ppm the results do appear linear but deviate from linearity with increasing concentration. This non-linear response agrees with earlier data taken at higher HCl concentrations. Fifteen ppm produced about the same percent response at 366°K as did 30 ppm at 400°K. This tends to support the idea of dipole-dipole, as van der Waal's interaction, and 350°K has been previously suggested as the optimum temperature range for these films.

One exposure was made with 15 ppm HCl in dry air at 366°K, resulting in an approximate 2% change in  $V_1$ , as had been noted in the last entry of Table 4-2. Therefore oxygen having no strong dipole moment, does not appear to block the response.

## APPENDIX

### Brief Review of Recent Work with $\text{MnO}_2$ Films

It is pointed out here that  $\text{MnO}_2$  film of only one thickness ( $\sim 200\text{\AA}$ ) was used in the present work. No detail measurements were carried out, but a quick survey was made to see the response of the  $\text{MnO}_2$  film to HCl exposure. A more careful investigation is in order to understand the behavior of these films.

### SAMPLE PREPARATION

$\text{MnO}_2$  was deposited by radio frequency (RF) sputtering on #7059 Corning Glass substrates. The glass substrates were ultra-sonically cleaned in a solution of 10%  $\text{H}_2\text{O}_2$  and 80% deionized water, followed by degreasing in Trichloroethylene and Acetone baths and were stored in methanol, prior to their use and were blown dry in nitrogen.

$\text{MnO}_2$  films were sputtered in an argon atmosphere at 7.75 mTorr pressure and at 50W total target power for 7 minutes. The substrate was water-cooled during the deposition. About  $200\text{\AA}$  thick, very light brown transparent films were obtained on glass substrates. Gold contacts were thermally evaporated on top. The device geometry is similar to the one shown in Figure 3.4-1.

### RESULTS

The resistance of the film was measured in a nitrogen atmosphere and was found to be dependent on the nitrogen flow rate. Figure 5.1 shows the value of the film resistance for varying  $\text{N}_2$  flow rates at  $300^\circ\text{C}$ . From this figure, increasing  $\text{N}_2$  flow rate seems to first increase and then slightly decrease the film resistance. The film was exposed to HCl concentration of 1000 ppm in a 3.0 l/min nitrogen flow. The film

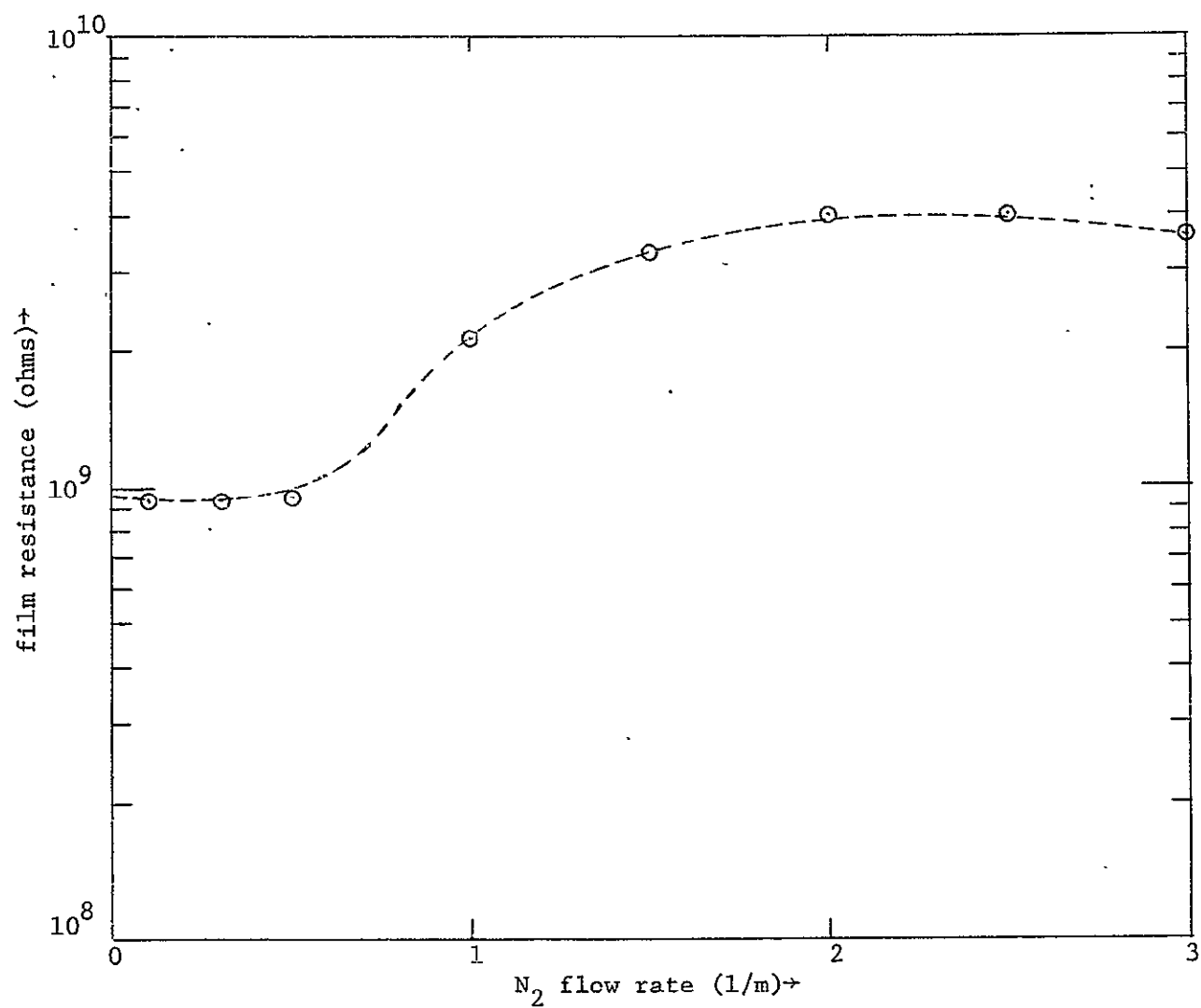


Figure 5.1. Variation of  $\text{MnO}_2$  film resistance with  $\text{N}_2$  gas flow rate at  $300^\circ\text{C}$ .

Resistance showed a large decrease (change in conductance being almost 200%) on this first exposure to HCl. However, subsequent exposures to the same HCl concentration showed successively smaller changes in the film resistance (successive changes in conductance being only 26.3% and 9.4%). Along with this change in the response, the film resistance, upon exposure to HCl, failed to come back to its value prior to the exposure indicating perhaps a permanent change in the film property or an incomplete HCl desorption.

The film response was then studied at an  $N_2$  flow rate of 0.5 l/min. First the response to 6000 ppm HCl in  $N_2$  background was studied at three different temperatures. Table 5.1 gives the results of these observations. From this table, 300°C appears to be a convenient temperature for operation of this detector.

Figure 5.2 shows the percent change in the film conductance as a function of HCl concentration in 0.5 l/min.  $N_2$  flow rate at 300°C. Here the film was first exposed to 6000 ppm HCl concentration in  $N_2$  and subsequently the concentration of HCl was increased in the incremental steps of 4000 ppm. The change in conductance of the film due to the last two incremental steps is seen to be linear. However, the response to the entire HCl concentration is not linear. A possible reason for this, among other things, may be the past history of the film. A change in film resistance was observed after HCl exposure. Perhaps a long time for desorption may be necessary in this case. Due to lack of time this was not investigated. Also, higher temperatures may speed up the desorption process. However, heating the sample to 325°C for 15-20 minutes did not seem to help in the present case.

Figure 5.3 shows the time response of the film after exposure to 6000 ppm HCl in 0.5 l/min.  $N_2$  flow rate at 300°C. The response time is

Table 5.1. Total and percent changes in the film conductance as a function of three different temperatures on exposure to 6000 ppm HCl in 0.5 l/m N<sub>2</sub> gas flow.

Temp.	Film conductance in 0.5 l/m N <sub>2</sub> gas flow (ohm) <sup>-1</sup>	Film conductance in 6000 ppm HCl in 0.5 l/m N <sub>2</sub> gas flow (ohm) <sup>-1</sup>	$\Delta\sigma$ (ohm) <sup>-1</sup> (change in film conductance)	$\Delta\sigma\%$ (percent change in film conductance)
275°C	$4.88 \times 10^{-10}$	$1.12 \times 10^{-9}$	$6.32 \times 10^{-10}$	131%
300°C	$1.7 \times 10^{-9}$	$4.74 \times 10^{-9}$	$3.04 \times 10^{-9}$	179%
325°C	$5 \times 10^{-9}$	$8.77 \times 10^{-9}$	$3.77 \times 10^{-9}$	75.4%

less than five minutes and may be slightly improved by decreasing the time constant of the measuring equipment. Figure 5.4 shows the desorption time on shutting off 18000 ppm HCl in 0.5 l/min. N<sub>2</sub> flow at 300°C. The value of the sample conductance before HCl exposure was  $2 \times 10^{-9}$  (ohms)<sup>-1</sup>.

Though not accurately measured, slight increase in sample conductance was obtained by exposure to 8 ppm HCl in N<sub>2</sub> at 0.5 l/min. flow rate. However, after the initial response the film did not desorb for a long time making it insensitive to subsequent 8 ppm HCl in N<sub>2</sub> exposures. No detail measurements on the response of this film to HCl in a dry air background were made. However, a slight increase (1-2%) in resistance of the sample was seen on exposure to 16 ppm HCl in 0.2 l/min. flow of dry air at 270°C.

System Limitations: With the existing set up HCl concentration between 10 ppm and 6000 ppm could not be accurately obtained for an N<sub>2</sub> flow of 0.5 l/min. or smaller. Changes in the flowmeters and the gas flow design technique are needed to cover the intermittent ranges of importance.

At present, the noise due to the temperature controller is the limiting system noise and must be removed once more sensitive measurements are required.



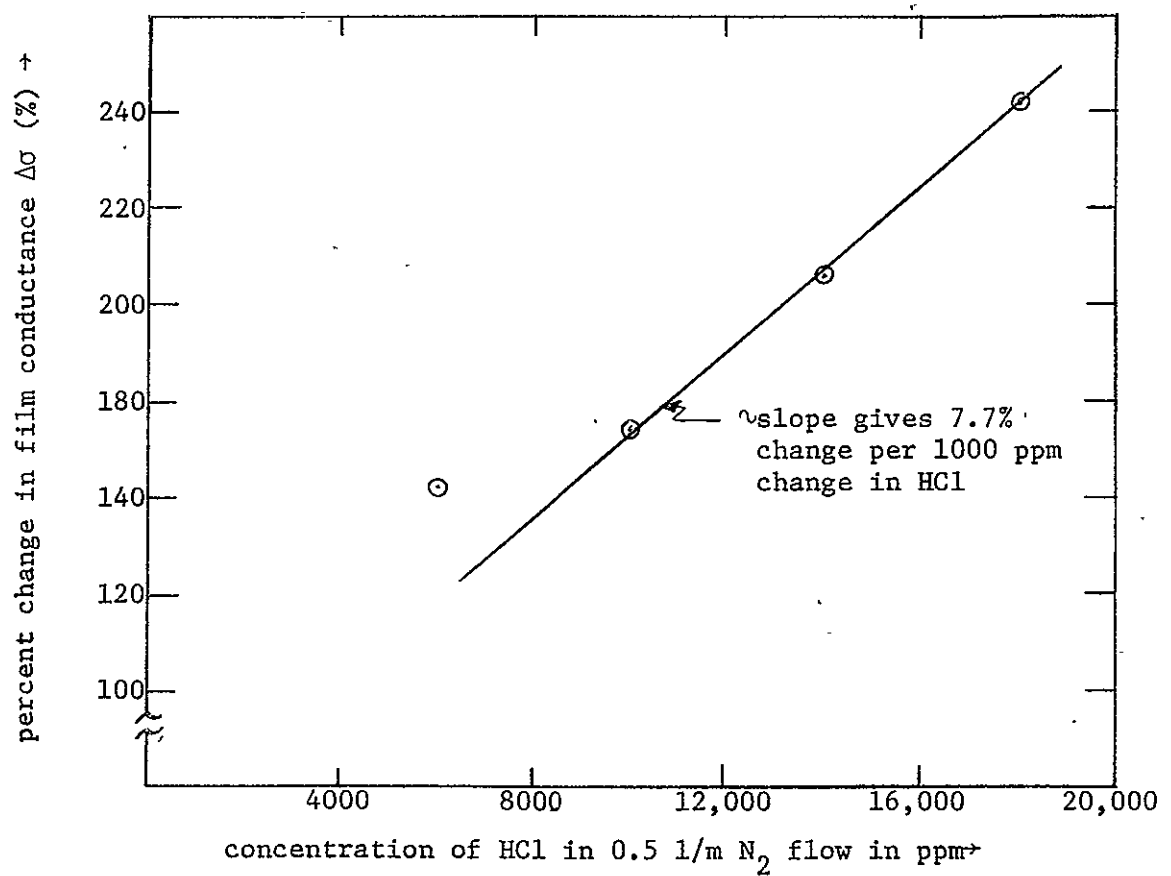


Figure 5.2. Percent change in the film conductance as a function of HCl concentration in 0.5 l/m  $N_2$  flow at 300°C.

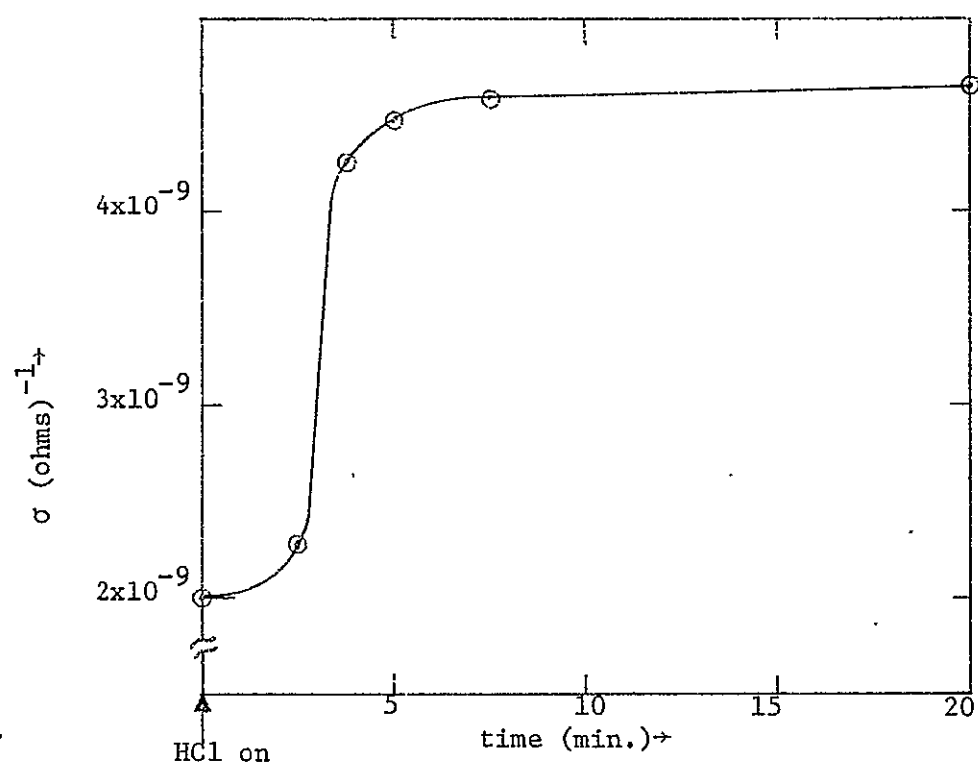


Figure 5.3. Change in the film conductance  $\sigma$  with time on exposure to 6000 ppm HCl in 0.5 l/m.  $N_2$  flow at 300°C.

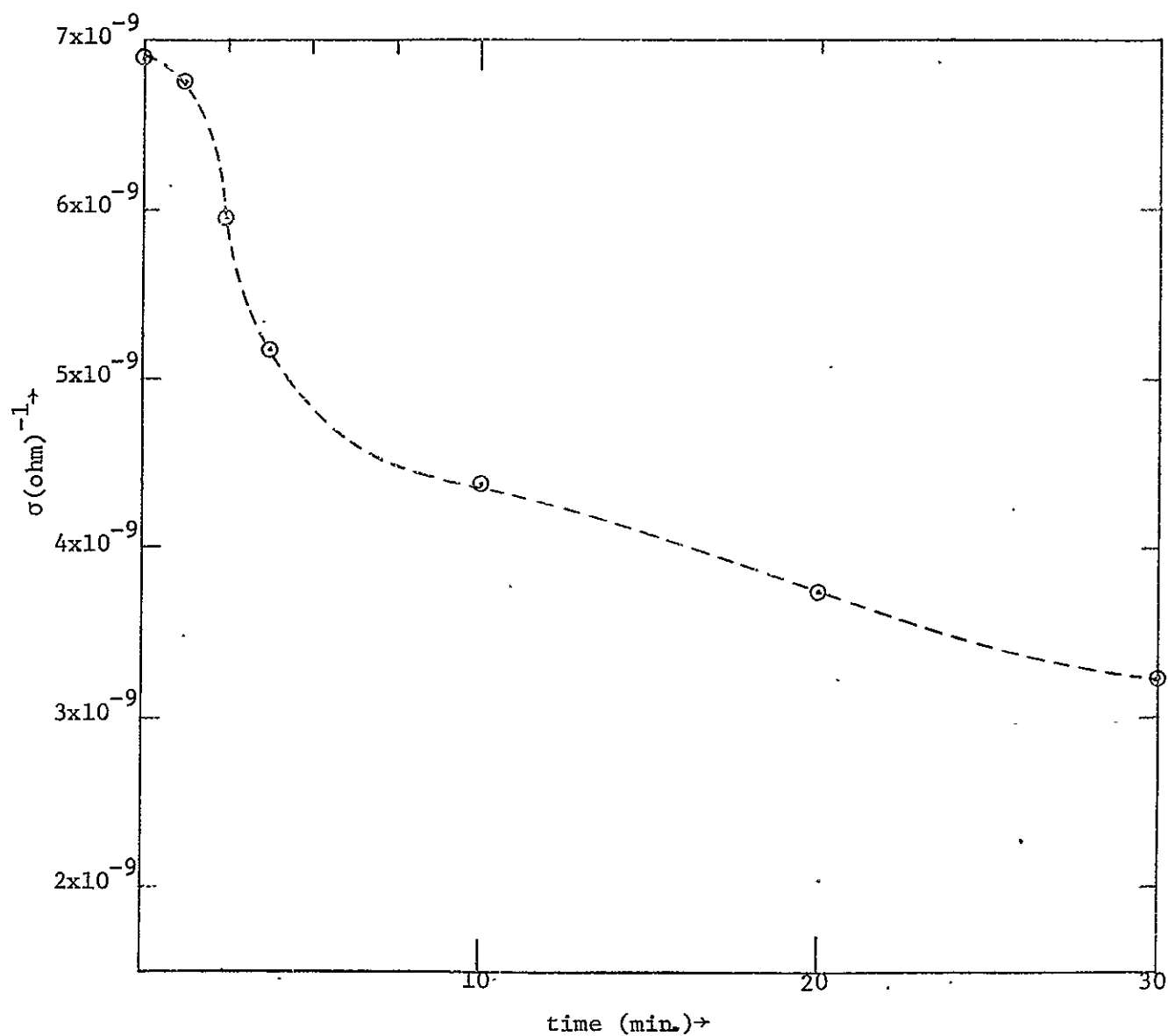


Figure 54. Change in the film conductance  $\sigma$  with time on shutting off 18,000 ppm HCl in 0.5 l/m  $\text{N}_2$  flow at  $300^\circ\text{C}$ .

## DISCUSSIONS

This work is just an initial phase of a more comprehensive work necessary to determine the possibility of using  $\text{MnO}_2$  as thin film HCl sensors. From the results of the experiment carried out here, the practical application of sputtered  $\text{MnO}_2$  films as HCl gas detectors can be neither confirmed nor denied. The  $\text{MnO}_2$  surface is definitely responsive to HCl gas. However, the  $\text{MnO}_2$ -HCl system suffers from the point of view of repeatability — perhaps arising from the failure of the  $\text{MnO}_2$  film to recover to its initial state after being exposed to HCl. The answer to the use of  $\text{MnO}_2$  as a practical sensor may lie in the understanding of physical phenomena responsible for the above. A more complete understanding can only be obtained by further experimentation including annealing studies, Hall measurements in desired environments and response, among other things, as a function of temperature and thickness of the samples.

## 6. Summary and Recommendations

The primary results of the first phase to develop a thin film sensor for gaseous HCl are:

1. Thin films of silver chloride can be prepared by vapor deposition whose chemical and physical properties are suitable for an HCl sensor,
2. thin films of silver chloride do exhibit modulation of surface conductivity with the adsorption of HCl onto the surface of the film,
3. the response can be enhanced by controlling the impurities introduced into the film during vapor deposition,
4. a change in conductivity can be observed when the silver chloride films are introduced to tens of parts per million HCl,
5. the response time (the time for the conductivity reaches a steady value after the introduction of HCl) is the order of a few minutes,
6. the measurement of changes in conductivity are not limited by noise from the sensing element (AgCl thin film).

Regarding the advisability to proceed to phase two of the development of a thin film sensor of HCl, there still remains the issue of specifying the criteria on which the judgment should be based. It is our recommendation that phase two be postponed until the parameters of the environment in which the sensor must operate are established. In the absence of this information we can simply conclude that it appears feasible to build a thin film HCl sensor which responds reproducibly to gaseous HCl in the 10-100 ppm range. Interference effects from water can be negated by operating at an elevated temperature. Interference effects from gases such as CO and NO<sub>x</sub> are unknown. Molecular oxygen does not appear to be a problem.

Should the environmental parameters become available, we are prepared to undertake a preliminary design of a thin film sensor system to be evaluated prior to entering phase two. Assuming the preliminary design is judged acceptable we are prepared to proceed with phase two of the development of a thin film sensor for gaseous HCl.

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